QC
1
I42

REGISTERED No. BG. 315

MICHIGAN
25 1961
PHYSICS
LIBRARY

PROCEEDINGS

OF THE

INDIAN ACADEMY OF SCIENCES

VOL. LIII] *SECTION A* [No. 6

JUNE 1961

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY T. K. BALAKRISHNAN
SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF
SCIENCES, BANGALORE

ON THE POSSIBILITY OF A NEW PHASE-DETERMINING METHOD APPLYING THE MÖSSBAUER EFFECT

By R. Srinivasa Raghavan

(*Tata Institute of Fundamental Research, Bombay-5, India*)

Received February 8, 1961

(Communicated by Dr. B. V. Thosar)

Introduction

The technique of recoil-less absorption and emission of soft γ-rays in crystals (Mössbauer effect) has been shown to have widespread applications in many fields of research. This paper describes its possible use as a means for determining the phases of the Bragg reflections of the incident γ-rays, from crystals containing the resonance isotope in which the γ-rays can be absorbed and re-emitted without recoil.

The resonance scattering of nuclear γ-rays was a difficult problem prior to 1958, because, during absorption or emission the recoil of the residual nucleus created enough energy loss in the γ-ray, to throw it off resonance from the sharp nuclear excited states. Recently, however, it was shown[9] (Mössbauer, 1958) that under suitable conditions, for a fraction of the emission or absorption processes the recoil was taken up by the crystal as a whole instead of by the individual nucleus and so the γ-ray had the full energy. This increased the cross-section for resonance to a very high value. It was also found that by adding or subtracting small amounts of energy of the order of the width of the excited state (accomplished simply by moving the source of γ-rays with respect to the scatterer with velocities of the order of cm./sec.) the resonance could be destroyed. The shape of the resonance could also be traced by using a range of velocities. The average cross-section for recoil-less resonance scattering can be shown to be[14] (Visscher, 1960)

$$\sigma = 2\pi\lambda^2 \frac{1}{(1+\alpha)^2} \frac{\Gamma^2}{(S^2+\Gamma^2)} \frac{(2I_e+1)}{2(2I_g+1)} e^{-2g}$$

$$= \sigma_0 \frac{(2I_e+1)}{2(2I_g+1)} e^{-2g}$$

where Γ is the total width of the excited state, α the total internal conversion coefficient, λ the reduced wavelength of the γ-ray and I_e and I_g are the

spins of excited and ground states respectively. $S = vE_0/c$, where v is the relative velocity between the source and the scatterer, E_0 the energy of transition and c the velocity of light. e^{-2g} is the Debye-Waller factor which gives the fraction of transitions occurring without recoil.

THE COHERENCE QUESTION

In the presence of such recoil-less nuclear resonance scattering, the other important elastic scattering processes that occur are, (*a*) Thomson scattering by the nucleus and (*b*) Rayleigh scattering by the electrons of the atom. Since all the three scattering modes are elastic, the question of coherence between these may be considered. The coherence of the Thomson and Rayleigh scattering has been discussed[6-7] (Moon, 1950, 1960) and also experimentally verified[13] (Sood, 1958). For the nuclear resonance scattering also to be coherent[4] a chief requirement is that the incident line should be very sharp as compared to the absorption line[2] (Heitler, 1944). When artificial methods are employed to compensate for recoil losses by broadening the incident line enough to overlap with the absorption line, the resulting resonance process cannot be expected to be coherent, because this inherently involves an incident line broader than the absorption line. Further, recoil and thermal movements will produce random fluctuations in phase. However, when recoil-less resonance is produced, the scattering is truly elastic, without change even in the vibrational states of the crystal, producing emission and absorption lines of equal widths. Although here, random sources of incoherence are eliminated we still cannot expect complete coherence. An estimate[8] of the degree of coherence in a resonance process, like the Mössbauer effect, may be made by considering the incident radiation as a damped harmonic vibration with its characteristic frequency and decay constant, falling on a resonator with similar constants of its own. The differential equation of motion of this system yields a transient solution with the characteristics of the resonator, and a steady state solution with those of the incident radiation and coherent with it. The ratio of the time averages from $t = 0$ to $t = \infty$ of these two solutions is a measure of the degree of coherence. This ratio directly involves the widths of the incident and absorption lines and if these are equal we can expect the scattering to be about 50% coherent.

Under these conditions, the total scattering amplitude from an atom may be written as a coherent sum of all modes of scattering, *i.e.*,

$$a_{\text{compound}} = \{a_{\text{ray}} + a a_{\text{res.}}\}$$

where

$$a_{ray} = f(e^2/mc^2)\, e^{-M},$$

f being the atomic scattering factor, (e^2/mc^2) the classical electron radius, e^{-M} the root of the Debye-Waller factor used in crystallography, representing the reduction of Rayleigh peak intensity at Bragg angles due to thermal motion of the atoms, and $a_{res} = \sqrt{\sigma_0}\, e^{-\vartheta}$. Here the Thomson scattering amplitude has been neglected in comparison with the other two. α is the degree of coherence in the resonance process. This can be used as the basis for describing the total coherent scattering from a macroscopic crystal, but here other sources of incoherence enter. First, the resonance isotopes are only a fraction of the different stable isotopes that go to make the element in the crystal, and these are situated at random. If β is the abundance of the resonance isotope in the crystal, then the average coherent scattering amplitude can be written as:

$$a_{coh.} = (1 - \beta)\, a_{ray} + \beta a_{com.}$$

In the same way, the statistical probability factor

$$\gamma = \frac{(2I_e + 1)}{2(2I_g + 1)}$$

should also be included in the expression for $a_{coh.}$ Then

$$a_{coh} = (1 - \beta\gamma)\, a_{ray} + \beta\gamma a_{com.}$$

$$= \left\{ f\left(\frac{e^2}{mc^2}\right) e^{-M} + \alpha\beta\gamma \sqrt{\sigma_0}\, e^{-\vartheta} \right\}.$$

The total scattering is

$$(1 - \beta\gamma)\, |\, a_{ray}\, |^2 + \beta\gamma\, |\, a_{com.}\, |^2$$

so that the incoherent background is given by

$$\beta\gamma\,(1 - \beta\gamma)\, |\, a_{com.} - a_{ray}\, |^2.$$

The isotopic and spin incoherences have been treated as in the case of the scattering of slow neutrons in crystals.

The total Rayleigh scattering amplitude from all the atoms (considering them to be the same for simplicity) in the unit cell of a crystal is given by the structure factor

$$F_{hkl} = \sum_j f\, e^{-M} e^{2\pi i\,(hx_j + ky_j + lz_j)}$$

where $x_j y_j z_j$ are the fractional co-ordinates of the j-th atom. The intensity of the reflection (hkl) where h, k and l are the Miller indices of the reflecting plane is proportional to $|F_{hkl}|^2$. With the resonance scattering also present it will instead be proportional to $|F'_{hkl}|^2$, where

$$F'_{hkl} = \sum_j a_{coh} \cdot e^{2\pi i (hx_j + ky_j + lz_j)}.$$

This shows that under these conditions there will be a greater intensity in the Bragg peaks due to the coherent addition of the Rayleigh and resonant scattering. The background intensity is also increased due to the additional incoherent scattering.

APPLICATION TO THE PHASE PROBLEM

As a result of the compound scattering, the intensity of the Bragg peaks can be increased to a limit by adding variable amounts of the resonance amplitude to the electronic amplitude. a_{coh} can be changed very precisely by varying the relative velocity between the source and the scatterer (*i.e.*, by varying S in the denominator of σ_0). This changes the amplitude as well as the phase of the resonance scattering which is $\pm\pi$ at the extreme wings and $\pi/2$ at exact resonance, resulting in the compound scattering having a phase angle different from the usual 180° as for pure electronic scattering. This should, therefore, lead to the violation of Friedel's Law, since the imaginary term in the resonance denominator will give unequal values for $|F'_{hkl}|$ and $|F'_{\bar{h}\bar{k}\bar{l}}|$ and so unequal intensities for these reflections. The possibility of having a complex scattering factor involving the breakdown of Friedel's Law can be compared to the situation arising out of the anomalous dispersion[3] (James, 1954) of X-rays by the K-electrons. The two are similar, one being a nuclear resonance and the other an atomic resonance.

The complex structure factor can be written as $|F_{hkl}| e^{i\phi}$ where $|F_{hkl}|$ is the structure amplitude and ϕ is the phase constant. Measurement of intensities of reflections gives only $|F_{hkl}|$ and information of ϕ is lost. To make a Fourier synthesis of the structure factors and hence to derive the structure of the crystal it is necessary to know F_{hkl} and not merely $|F_{hkl}|$. So the problem of finding ϕ for each reflection is known as the phase problem. The general principle of any phase determining method[5] (Lipson and Cochran, 1957) is that we can deduce the phase constants by a study of the change in the intensity of reflections when the scattering factor of a particular atom is varied in a preferential and known manner. Usually, the isomorphous replacement,[5] or the anomalous dispersion methods[10–12] (Ramachandran and Raman, 1956; Pepinsky and Okaya, 1956) are used

for this purpose. In the former method only a change in the scattering amplitude is made while in the latter, the phase of scattering is changed as well, leading to the breakdown of Friedel's Law. In some cases the latter method alone is not found to be sufficient and a combined use of both these methods has been suggested. It is obvious that any method by which the scattering factor can be easily changed with change in phase as well as amplitude resulting in the violation of Friedel's Law can be applied in the same way as the anomalous dispersion method. The recoil-less resonance method would then fill these needs adequately and may therefore be used for the determination of phases, and also the absolute configuration of crystals. It is worthwhile pointing out that where it can be used, the new method can be more advantageous, since by the simple artifice of having two or three velocities of the source or the scatterer, the resonance amplitude and hence the compound amplitude can be changed considerably. Measurement of the intensities of inverse reflections with these velocities may help fix the phase constant without ambiguity even in cases where previously the anomalous scattering method alone was not sufficient. This is mainly because of the fact that the change in the f value due to anomalous dispersion is fixed, and even if it can be changed slightly one has to use different radiations which may not always be possible. Use may also be made of the fact that in the new method, there is provision to make the compound scattering factor of the resonance atom even negative by using velocity of the correct sign. This is comparable to some cases in neutron diffraction where, again due to the action of resonance, the scattering factor becomes negative.

The success of the method may depend largely on the extent to which the coherent peaks can be distinguished from the considerable amount of incoherent background which should be expected. For this it may be necessary to use crystals enriched in the resonance isotope. Also, strong sources may be indispensable to provide geometries good enough to resolve the Bragg peaks. However, the method even if practicable, is of limited scope, since only Mössbauer transitions involving a γ-ray wavelength ≈ 1 Å would be useful. Of the cases reported so far, the 14·4 Kev. line in the decay of $Co^{57} \rightarrow Fe^{57}$ made famous by spectacular experiments in many fields, may be most useful. In this case, rough estimate of the cross-sections are given in Table I (Appendix). Here the resonance parts have been calculated for zero relative velocity between source and absorber. The enhancement of the coherent cross-section with enrichment is evident. Also, the magnitude of the imaginary part ($\alpha\beta\gamma\sqrt{\sigma_0}\, e^{-\vartheta}$) of a as compared to its real part, *viz.*, $f(e^2/mc^2)$ which determines the difference in intensities

$|F'_{hkl}|^2$ and $|F'_{\bar{h}\bar{k}\bar{l}}|^2$ is seen to be quite large. This compares favourably with the X-ray anomalous diffraction method where the imaginary addition $\Delta f''$ is usually much smaller than f. Hence these differences in intensities should be measurable in experiments with compounds of iron using Fe^{57} radiation.

The first experiment for testing the interference between Rayleigh and Resonance scattering has been performed[1] (Black and Moon, 1960) using the Fe^{57} radiation. Although there seems to be some evidence of this, it should be desirable to have further confirmation by a direct investigation on the enhancement of Bragg peaks due to this interference of the two processes.

SUMMARY

When soft γ-rays are emitted without recoil, the radiation emitted has a considerable fraction contained within the natural line-width. This part of the radiation is expected to be partially coherent with the incident γ-rays and so with the Rayleigh scattered component. Under these conditions the total scattering amplitude will be a sum of the Rayleigh and Resonance amplitudes. This coherent addition leads to an enhancement of the intensities of Bragg reflections from the crystal. Since the total amplitude is complex, the intensities of inverse reflections will be unequal. It is suggested that this possibility be utilised, as in the similar case of anomalous dispersion of X-rays, for determining the phase constants as also the absolute configuration of crystals. Practical limitations are discussed.

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. B. V. Thosar and Dr. S. Jha for their keen interest and encouragement, and to Professor G. N. Ramachandran for reading the manuscript and for some helpful comments. He is also very grateful to Professor P. B. Moon for clarification of some ideas.

REFERENCES

1. Black, P. J. and Moon, P. B. *Nature*, 1960, **188**, 481.
2. Heitler, W. .. *Quantum Theory of Radiation*, Oxford University Press, 1944, Chapter III.
3. James, R. W. .. *Optical Principles of X-Ray Diffraction*, G. Bell & Sons, 1954
4. Kastler, A. .. *C.R. Acad. Sci.*, 1960, **250**, 509.
5. Lipson, H. and Cochran, W. *Determination of Crystal Structures*, G. Bell & Sons, 1957, p. 140.

6. Moon, P. B. .. *Proc. Phys. Soc.*, 1950, **63 A**, 1189.
7. ———— .. *Nature*, 1960, **185**, 429.
8. ———— .. Private Communication.
9. Mössbauer, R. L. .. *Zeits. f. Physik*, 1958, **151**, 124.
10. Okaya, Y. and Pepinsky, R. *Phys. Rev.*, 1956, **103**, 1645.
11. Pepinsky, R. and Okaya, Y. *Proc. Nat. Acad., Sci., U.S.*, 1956, **42**, 286.
12. Ramachandran, G. N. and Raman, S. *Curr. Sci.* 1956, **25**, 348.
13. Sood, B. S. .. *Proc. Roy. Soc.*, 1958, **247 A**, 375.
14. Visscher, W. M. .. *Annals of Physics*, 1960, **9**, 194.

APPENDIX

TABLE I

	$\lvert a_{ray}\rvert^2 = f^2\left(\frac{e^2}{mc^2}\right)^2$ (cm.^{2})	$\sigma_{res.} = \sigma_0 e^{-2\varrho}$ (cm.^{2})	$\sigma_{coh.} = \lvert a_{coh.}\rvert^2 = \left\lvert f\left(\frac{e^2}{mc^2}\right) + \alpha\beta\gamma\sqrt{\sigma_0}\, e^{-\varrho}\right\rvert^2$ (cm.^{2})	$f\left(\frac{e^2}{mc^2}\right)$ (cm.)	$\alpha\beta\gamma\sqrt{\sigma_0}\, e^{-\varrho}$ (cm.)
Natural iron 2% Fe^{57}	5×10^{-23}	$1{\cdot}84\times10^{-21}$	$6{\cdot}8\times10^{-23}$	7×10^{-12}	$4{\cdot}3\times10^{-12}$
Iron enriched to 60% in Fe^{57}	5×10^{-23}	$1{\cdot}84\times10^{-21}$	$1{\cdot}7\times10^{-20}$	7×10^{-12}	$1{\cdot}3\times10^{-10}$

ELECTRON SPIN RESONANCE STUDIES OF THE FREE RADICALS DERIVED FROM TETRAPHENYLHYDRAZINE

By M. Ramachandra Das, Arvind V. Patankar
and
Balu Venkataraman

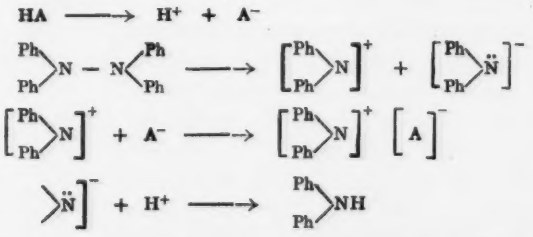
(*Atomic Energy Establishment, Trombay and Tata Institute of Fundamental Research, Bombay*)

Received September 21, 1960

(Communicated by Dr. S. S. Dharmatti, F.A.Sc.)

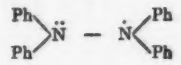
Introduction

Wieland prepared tetraphenylhydrazine for the first time and proposed that: (1) when heated in a non-polar solvent like xylene or toluene to about 90° C., tetraphenylhydrazine dissociates into diphenylamino-radicals, and (2) the coloured compounds formed by the action of acids on tetraphenylhydrazine have a quinonoid structure.[1] Weitz and Schwecten observed that tetraphenylhydrazine does not form salts with acids unless oxidizing agents are present and hence suggested that the action of acids on tetraphenylhydrazine produces free radicals instead of quinonoid compounds.[2] Lewis and Bigeleison held the view that in solution tetraphenylhydrazine is in dynamic equilibrium with the positive and negative ions of diphenylnitrogen and, when an acid is added, the negative ions are first removed by protonation; the positive ions which accumulate combine with the anion of the acid[3]:



The action of ultra-violet rays on tetraphenylhydrazine held in a rigid medium was studied by Lewis and Lipkin and the following reactions were

postulated: (1) photodissociation forming two molecules of diphenylamino radicals, (2) photoionization resulting in the formation of positive and negative diphenylamino ions, and (3) photo-oxidation resulting in the formation of the tetraphenylhydrazyl radical,[4]



The technique of electron spin resonance spectroscopy was employed by Hoskins to investigate this problem. He attempted to observe the paramagnetic resonance of diphenylamino radical, which is presumably obtained by heating to 90° C. a solution of tetraphenylhydrazine in toluene.[5] A five-line spectrum contrary to an expected three-line spectrum was obtained; it will be seen later that an impure sample of tetraphenylhydrazine gives a five-line spectrum in the solid state and in xylene.

The present investigations on free radicals obtained from tetraphenylhydrazine under different conditions extend Hoskins' attempts to identify the diphenylamino radical. Electron spin resonance has proved very useful in the study of many organic free radicals, and the rich hyperfine structure found in the resonance spectra of many organic free radicals has been the subject of considerable theoretical and experimental studies.[6] This work was undertaken with the expectation that the several radicals obtained from tetraphenylhydrazine could be distinguished from one another with the help of the hyperfine structure in their resonance spectra and their *g*-values.

TECHNIQUES AND MATERIALS

The Spectrometer.—The electron paramagnetic resonance studies were carried out in an *x*-band reflection cavity spectrometer consisting of a Varian V–4500–40 *x*-band microwave bridge, the Varian klystron power supply (V–4500–20) and their klystron control unit (V–4500–10); the low frequency magnetic field modulation for derivative recording was provided by a 37 cps. oscillator and power amplifier; the output of a twin-tee narrow band amplifier was detected with a phase-sensitive detector and recorded on a Honeywell-Brown strip chart recorder to obtain the derivative spectrum. The frequency of the klystron was stabilized with the sample cavity as reference; the klystron was frequency modulated by impressing a 10 kcs. modulation on its reflector voltage and the 10 kcs. component of the output of the microwave crystal diode, 1N23B, was detected with a phase-sensitive detector and used for the frequency stabilization of the klystron.

A Varian V–4012–A 12″-electromagnet with its associated V–2100–A power supply and a voltage regulator (V–2101–C) provided the magnetic

field for the resonance studies. The magnetic field was scanned linearly at a constant microwave frequency for obtaining the resonance spectra.

Measurement of magnetic field strength.—The magnetic fields were measured in terms of the proton magnetic resonance frequencies using a circuit of the type described by Knoebel and Hahn,[7] with mineral oil as the sample; the probe containing the mineral oil was placed as close to the paramagnetic sample as possible. The proton resonance frequency was measured with the aid of a loosely coupled antenna placed inside the proton oscillator box, followed by a tunable radio frequency amplifier. The output of the amplifier was fed into a Hewlett Packward frequency converter (hp-525–A) and counter (hp-524–B) combination. The error in the proton resonance frequency due to dispersion effects was measured by following, on the frequency counter, the changes in the oscillator frequency as the magnetic field passed slowly through resonance; it was found to be less than ± 40 cps. in 14 mcs. (*i.e.*, about 3 parts in 10^6). In order to minimise the errors due to dispersion, care was taken that the magnetic field did not drift during the period of measurement of the proton resonance frequency; the measurements were made only after allowing an initial warm up period of about 2 hours for the magnet and magnet power supply to stabilize. After making a series of measurements, the corrections to be applied for the difference between the magnetic field strengths at the proton probe position and the position of the paramagnetic sample were determined by removing the microwave cavity from the magnetic field and shifting the proton probe to the position originally occupied by the paramagnetic sample. The proton probe was easily reset at these two positions with the help of markings on an aluminium plate on which the proton oscillator box rested. This procedure could be followed very easily because of the high stability of magnetic fields attainable with the Varian 12″magnet and its power supply.

Measurement of microwave frequencies.—The microwave frequencies were measured by coupling a portion of the microwave power and beating it with the harmonics of a transfer oscillator.[8] This method is capable of measuring the microwave frequency to 1 part in 10^6, which is the accuracy of the counter.

g-*Value of DPPH.*—The g-value of α, α'-diphenyl-β-picryl hydrazyl (DPPH) was measured over several days to verify the accuracy of the method described above. When a speck of DPPH was used it was observed that though the ratio (ν_E/ν_P) of the electron spin resonance frequency for DPPH (ν_E) and the proton resonance frequency (ν_P) at the same magnetic field could be measured to a precision of 3 parts in 10^6 on

a single day, the values measured over several days varied about 2·5 parts in 10^4 (corresponding to a *g*-variation from 2·0033 to 2·0038). This variation was later found to be due to anisotropy effects derived from the sample not being truly polycrystalline. Over a whole day the orientation of the sample with respect to the magnetic field was left unchanged and hence the constancy of the results over a day. When the sample tube was rotated with respect to the field between successive measurements on a single day, the *g*-values were found to show variations of the same order as reported above.

The *g*-value of a 0·002 M solution of DPPH in xylene, which is not expected to show anisotropy effects, was measured over several days and the extreme variations of the ratio, (ν_E/ν_P), were within 2 parts in 10^5; the ratio was found to be $658{\cdot}6290 \pm 0{\cdot}0030$. The ratio of the proton magnetic moment in mineral oil to the proton magnetic moment in water is reported as $1{\cdot}0000041 \pm 0{\cdot}0000015$.[9] Combining this with the most recent value of the gyromagnetic rotio for protons in water, $\gamma_P = 2{\cdot}67513 \pm 0{\cdot}00002) \times 10^4$ gauss^{-1}sec.$^{-1}$,[10] the gyromagnetic ratio of protons in mineral oil is $(2{\cdot}67513 \pm 0{\cdot}00002) \times 10^4$gauss^{-1} sec.$^{-1}$ The *g*-value for DPPH is given by

$$g = \frac{\frac{\nu_E}{\nu_P}}{\frac{e}{2mc\gamma_P\,(\text{mineral oil})}}$$

and with $(e/mc) = (1{\cdot}75887 \pm 0{\cdot}00003) \times 10^7$ e.m.u./gm.[11]

$$g\,(0{\cdot}002\ \text{M DPPH in xylene}) = 2{\cdot}00347 \pm 0{\cdot}00004.$$

The *g*-value for DPPH has been previously reported to be $2{\cdot}0036 \pm 0{\cdot}0003$.[12]

Measurement of g*-values,* hfs *spacings and line-widths of radicals other than DPPH.*—The *g*-values of the free radicals reported in this paper were measured by the method outlined for measurements on DPPH. The values obtained differ in their precision (as seen from Table I), depending on the line-width of the spectrum and the intensity of the paramagnetic resonance absorption that could be obtained. In all cases the derivative of the spectrum as seen on an oscilloscope was used to determine the centre of the absorption signal; whenever the sample gave a feeble absorption signal, the amplitude of field modulation was enhanced to several times the line-width in order to increase the ease of detection of the centre of the line. The amplitude of field modulation is known not to affect the position of the centre of the signal.

TABLE I

Electron spin resonance data on free radicals derived from and related to tetraphenylhydrazine

TABLE I

Electron spin resonance data on free radicals derived from and related to tetraphenylhydrazine

No.	Sample	Number of components	*g*-Values	Line-widths (gauss)[a]	*HFS* separations[b] Uncorrected (gauss)	*HFS* separations[b] Corrected (gauss)[c]	Total spread of the spectrum (gauss)	Remarks
I.	TETRAPHENYLHYDRAZINE (TPH)							
1.	TPH in xylene heated and cooled (Fig. 1)	3	2·00549 ± 0·00011	5·5	9·1	10	43	..
2.	TPH in xylene, kept for a week	3	2·00537 ± 0·00014	4·0 (approximate)	13	..	39	..
3.	TPH in acetic acid, heated and cooled (Fig. 2)	5	2·00284 ± 0·00010	3·4	6·1	6·8	41	..
4.	(a) TPH in acetic acid, shaken for ten minutes	..	2·00211 ± 0·00010	..	..	..	50	Very weak and poorly resolved
	(*b*) TPH in acetic acid, kept for a week	5	2·00285 ± 0·00005	4·2 (approximate)	7·6	..	43	..
5.	TPH in acetic acid + PbO_2 (Fig. 3)	5	2·00289 ± 0·00009	..	9·1	..	54	..
6.	TPH in concentrated sulphuric acid	5	1·9972 ± 0·0007	..	..	..	39	The radical is very unstable
7.	(*a*) TPH in acetic acid + sulphuric acid (green) Fig. 4 (*a*)	6 (?)	2·00184 ± 0·00011	..	5·7	..	51	..
	(*b*) TPH in CH_3COOD + sulphuric acid (green) Fig. 4 (*b*)	..	2·00169 ± 0·00007	..	..	..	43	Very poor resolution

TABLE I (*Contd.*)

No.	Sample	Number of components	*g*-Values	Line-widths (gauss)[a]	*HFS* separations[b]		Total spread of the spectrum (gauss)	Remarks
					Uncorrected (gauss)	Corrected (gauss)[c]		
II.	DIPHENYLAMINE (DPA)							
1.	DPA in acetic acid + PbO_2 (Fig. 5)	5	2·00289 ± 0·00010	2·9	7	..	37	..
2.	DPA oxidised with potassium permanganate and extracted with xylene (Fig. 6)	3	2·00416 ± 0·00010	..	..	..	45	..
III.	DIPHENYLBENZIDINE (DPB)							
1.	DPB in acetic acid + PbO_2 (Fig. 7)	5	2·00285 ± 0·00010	2·9	6·8	..	39	..
2.	DPB in xylene + AgO or PbO_2 (Fig. 8)	..	..	..	..	..	39	The spectrum is asymmetric and consists mainly of 3 lines

[a] The line-widths refer to distances between points of maximum and minimum slopes and are not correctedd for overlap.

[b] All the spectra [except III (2)] contained hyperfine components which were equally spaced, if overlap was taken into account.

[c] The corrections are made to take into account the overlap between the different hyperfine components; they are approximate and assume a Lorentzian shape for the individual hyperfine components.

The hyperfine structure separations were measured by observations on the oscilloscopes whenever possible. In most of the free radicals the line-widths were so large that the hyperfine structure separations could be obtained only from magnetic field marks put on the record of the spectra obtained with the strip chart recorder; and in certain cases only the overall spread of the spectrum could be estimated. Table I presents the data obtained on all the free radicals reported in this paper. The overlap corrections, whenever applied, are approximate and assume a Lorentzian shape for the individual hyperfine components. When making line-width and *hfs* separation measurements, the modulation amplitudes used were at least four times less than the estimated line-widths, so that the contribution to line-width from field modulation was negligible.

Materials

Tetraphenylhydrazine.—In the first few experiments a sample of tetraphenylhydrazine kindly sent to us by Dr. M. Vecera[13] was used. This sample, however, had turned green and gave an electron paramagnetic resonance spectrum by itself in the solid state and when dissolved in xylene. The sample was subjected to repeated crystallisations from a mixture of benzene and alcohol but failed to yield a colourless product.

A fresh sample of the material was prepared from diphenylamine by oxidation with powdered potassium permanganate.[14] On repeated crystalrsations from a mixture of benzene and alcohol, shining colourless crystals of tetraphenylhydrazine were obtained; these were dried under vacuum (M.P. 142° C. decomp.).

Diphenylbenzidine.—Diphenylbenzidine was prepared by the method described by Wieland.[15]

Deuterated acetic acid (CH_3COOD).—Deuterated acetic acid (CH_3 COOD) was prepared from acetic anhydride and 98% D_2O.[16]

Silver oxide.—Silver oxide was prepared by the oxidation of a solution of silver nitrate with potassium persulphate.[17]

The other chemicals were obtained commercially and were of ANALAR' grade.

Results and Discussion

I. Studies on tetraphenylhydrazine.—1. On heating a solution of freshly prepared, pure tetraphenylhydrazine in a non-polar solvent like xylene or toluene to about 90° C. the solution acquired a brownish green colour, which it retained on cooling to room temperature. The cooled

solution exhibited an electron spin resonance spectrum consisting of three lines with intensities in the ratio 1 : 1 : 1 (Fig. 1). A sample of tetraphenylhydrazine, which had turned green on keeping, gave, however, a resonance line even in the powder-form. The line from the powder exhibited fine structure, which was not very well resolved, and seemed to consist of at least five components. A solution of the sample in xylene gave a weak, five-line spectrum, which changed to a strong, three-line spectrum on heating. It must be pointed out, however, that not all samples of tetraphenylhydrazine showed visible decomposition on keeping; the samples obtained as colourless crystals after repeated crystallizations were not prone to decomposition on keeping.

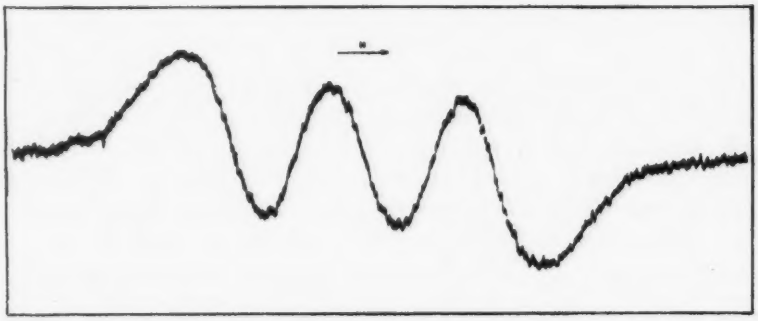


FIG. 1. Derivative of the electron spin resonance absorption from a solution of tetraphenylhydrazine in xylene heated to 90° C. and cooled. The radical is the diphenylamino radical, Ph-N-Ph.

The three-line spectrum obtained on heating a solution of tetraphenylhydrazine in a non-polar solvent is attributed to the diphenylamino radical,

(sometimes called diphenylnitrogen), whose formation was predicted by Wieland.[1] The hyperfine structure is believed to be due to the hyperfine interaction between the odd-electron and the spin of the N^{14} nucleus ($I = 1$), resulting in three equally spaced components with the same intensity.

2. If a solution of tetraphenylhydrazine in xylene was not heated, but allowed to remain for about a week, (or if oxygen was bubbled through the cold solution), the sample changed its colour slightly to a faint brownish hue and gave a weak resonance spectrum similar to Fig. 1. The *g*-value

also agreed with that of the diphenylamino radical within the limits of experimental error. The role of bubbled oxygen or atmospheric oxygen in this reaction is not well understood; it is possible that the first step in this reaction is oxidation, leading further to the cleavage of the molecule resulting in the formation of diphenylamino radicals.

3. A solution of tetraphenylhydrazine in acetic acid, however, showed an entirely different behaviour on heating or on keeping. On heating it turned violet and the cooled sample showed a very strong paramagnetic resonance absorption consisting of five lines (Fig. 2). The 5-line spectrum,

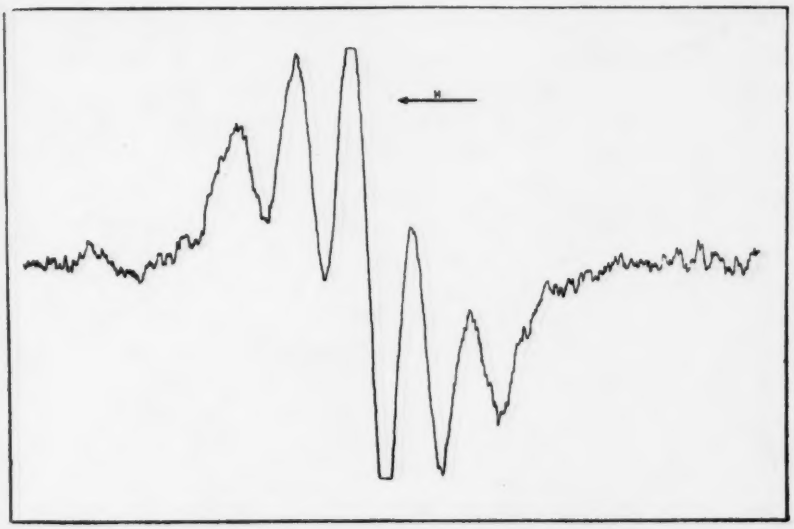
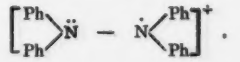
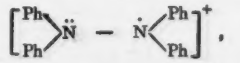


FIG. 2. Derivative of the electron spin resonance absorption from a solution of tetraphenylhydrazine in acetic acid heated and cooled. The radical is the tetraphenylhydrazinium radical,



which had a g-value that differs distinctly from that of the diphenylamino radical, is believed to be due to the radical of the type,



a radical similar to DPPH; the hyperfine structure arises from the interaction of the electron spin with the nuclear spins of the two equivalent nitrogen nuclei. The relative intensities of the hyperfine components also agree

qualitatively with the expected ratio of 1:2:3:2:1. The experiment was repeated with CH_3COOD and there was no change in the spectrum showing thereby that the fine structure does not arise from the protons derived from the carboxylic group of acetic acid.

4. When a freshly prepared solution of tetraphenylhydrazine in acetic acid was shaken for about ten minutes, the solution took a greenish tinge and showed a very poorly-resolved, weak, resonance absorption. The *g*-value of this differed from those of all the other spectra and the entire spectrum was spread over 50 gauss. A new radical species is formed, the nature of which could not be determined on account of the lack of detailed characteristics of the spectrum.

The same solution, however, when kept over for about a week turned dark brown and exhibited a strong, five-component, resonance line with a *g*-value agreeing with that of the radical obtained on heating a freshly prepared solution of tetraphenylhydrazine in acetic acid.

5. On oxidation of the solution of tetraphenylhydrazine in acetic acid with PbO_2, a strong absorption was obtained and the spectrum again showed five distinct lines, and its *g*-value agreed with that of the heated solution in acetic acid. The spectrum, however, was less resolved and was spread over a larger range; the spacing between the components was also different (*see* Fig. 3). The spectrum showed no change when CH_3COOD was used instead of CH_3COOH.

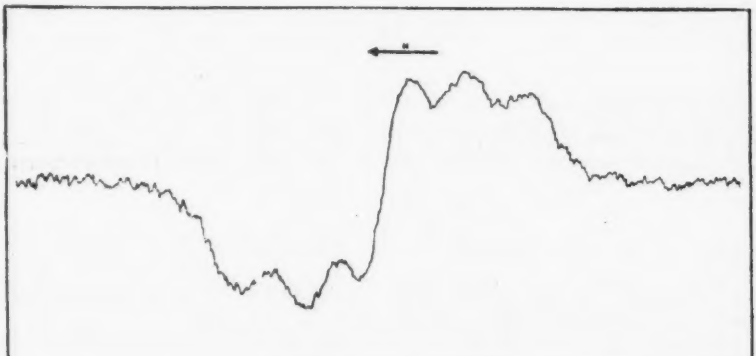


FIG. 3. Derivative of the electron spin resonance absorption from a solution of tetraphenylhydrazine in acetic acid treated with PbO_2.

6. A powdered sample of tetraphenylhydrazine, when treated with concentrated sulphuric acid, showed very rapid colour changes. There

was a deep violet colour that lasted for a very short time, followed by a longer blue which finally turned into pale green. All the colour changes were followed in the paramagnetic resonance spectrometer and only the violet phase showed the presence of free radicals. Initially, the concentration of radicals was very large but decreased very rapidly with no trace of resonance signal after ten minutes. The entire spectrum had to be scanned very rapidly using fast scanning techniques and short time constants. Steady flow techniques were not adopted because of certain experimental difficulties. The *g*-value measurements were made very hurriedly owing to the short life of the species and a precision greater than $\pm 0{\cdot}0007$ could not therefore be attained. The *g*-value was smaller than the free electron value of $2{\cdot}0023$ and the spectrum consisted of 5 components. Both the powdered tetraphenylhydrazine and the concentrated sulphuric acid were cooled to about $-5°$ C. before mixing to prolong slightly the life of the free radical phase.

7. The spectrum obtained from adding a drop or two of concentrated sulphuric acid to a freshly prepared acetic acid solution of tetraphenylhyrdazine was, however, very much different from those discussed earlier [Fig. 4 (*a*)]. When sulphuric acid was added to the acetic acid solution, there was a flash of violet colour followed quickly by blue, turning slowly into green. The violet phase was too short-lived for resonance studies and the blue phase exhibited no resonance. The green phase had a paramagnetic resonance spectrum, whose central portion showed a flat on the derivative curve indicating a trough rather than a peak at the centre. Since the hyperfine interaction with nitrogen ($I = 1$) alone cannot under any conditions give a trough at the centre, it had to be concluded that some hyperfine structure due to protons also was being observed. (In the other spectra where the observed *hfs* has been attributed solely to nitrogen nuclei, any *hfs* due to protons might be unresolved.) To confirm this, the experiment was repeated with CH_3COOD instead of CH_3COOH and the resulting spectrum [Fig. 4 (*b*)] showed no trough at the centre. The trough at the centre was, therefore, caused by hyperfine interaction with the protons derived from the carboxyl group of acetic acid; and the deuteration of the carboxyl group led to a peak instead of a trough, as expected from a nucleus with $I = 1$. The *g*-values of the deuterated and undeuterated species agree with each other, though they differ from the *g*-values of the other radicals and fall below the free electron value. The spectrum of the deuterated species was split into five main lines and the spectrum of the undeuterated species apparently into six. The five main lines might be due to a larger nitrogen splitting over which smaller proton or deuteron splittings are superimposed. From the fact that some of the *hfs* is derived from the proton abstracted

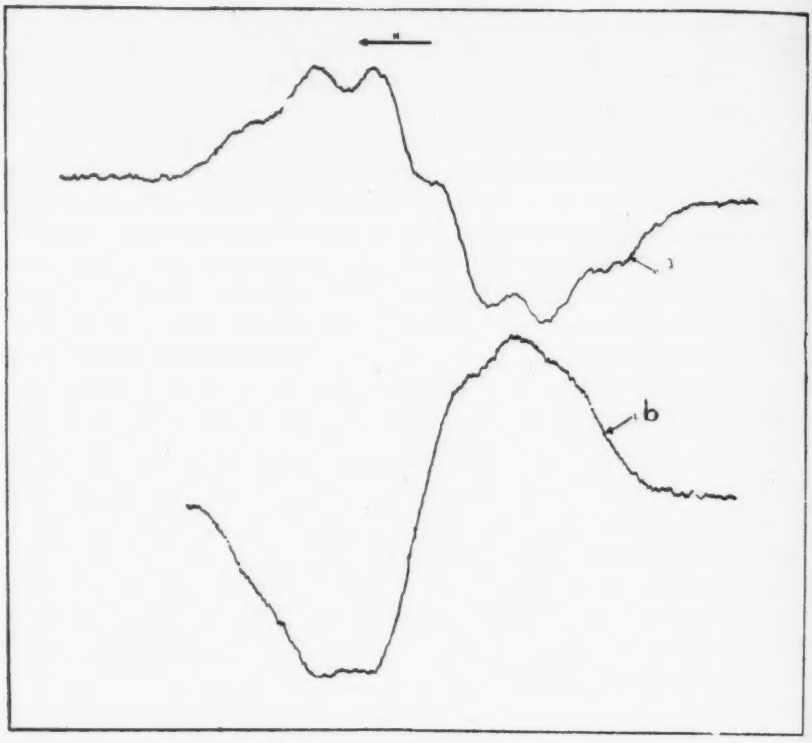


FIG. 4. (*a*) Derivative of electron spin resonance absorption from a solution of tetraphenylhydrazine in acetic acid treated with a drop of sulphuric acid; (*b*) CH_3COOD is used as the solvent instead of CH_3COOH.

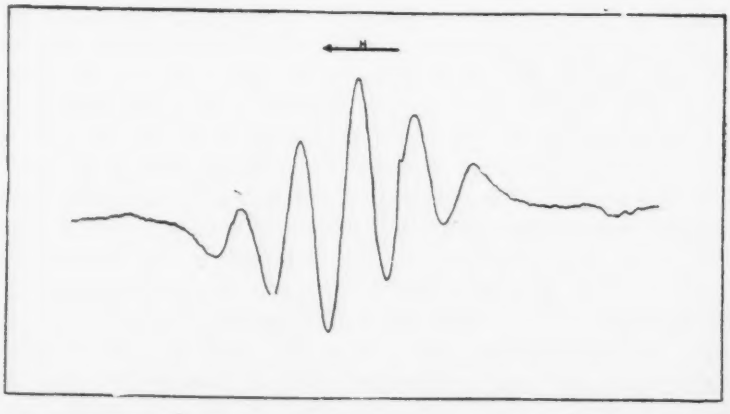
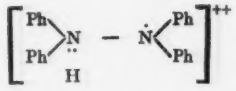


FIG. 5. Derivative of the electron spin resonance spectrum of a solution of dipyhenlamine in acetic acid treated with PbO_2. The radical is the same as that in Fig. 2.

from the carboxyl group of acetic acid, we are led to believe that the free radical formed is in all probability, the protonated tetraphenylhydrazinium radical,



II. Studies on Diphenylamine.—The paramagnetic resonance studies were extended to a few reactions of diphenylbenzidine and diphenylamine, to ascertain whether diphenylamine and diphenylbenzidine would, under suitable conditions, yield the same radicals as those obtained from tetraphenylhydrazine.

1. Diphenylamine was subjected to oxidation with PbO_2 in a polar medium, *viz.*, acetic acid. The resonance spectrum of the resulting mixture exhibited five components and the *g*-value, the line-widths of the components and *hfs* spacings agreed with those of the free radical obtained by heating a solution of tetraphenylhydrazine in acetic acid (Fig. 5). When deuterated acetic acid, CH_3COOD, was used there was no change in the spectrum.

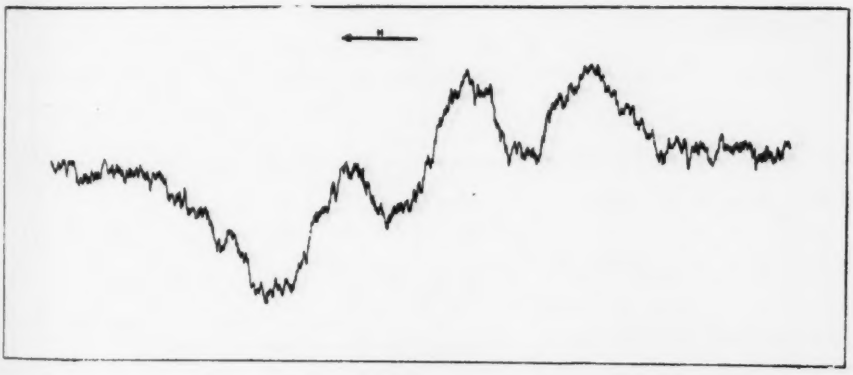


FIG. 6. Derivative of the electron spin resonance spectrum of the xylene extract of the residue obtained by the oxidation of diphenylamine with potassium permanganate in acetone and evaporating the acetone.

2. If, however, the oxidation was carried out with PbO_2 or AgO in xylene, a non-polar solvent, the resulting solution gave a very broad, weak resonance spectrum, whose characteristics could not be easily measured. Since, tetraphenylhydrazine is usually prepared by the oxidation of diphenylamine with powdered potassium permanganate in acetone this system

was subjected to resonance studies. A solution of diphenylamine in acetone was shaken for about ten minutes with powdered potassium permanganate at room temperature and the acetone was evaporated with a jet of nitrogen. The residue—which on crystallization from a benzene-alcohol mixture yields tetraphenylhydrazine—was extracted with xylene in the cold and the xylene extract was examined in the spectrometer; a well-resolved three-line spectrum was found (Fig. 6). This spectrum resembled the spectrum of diphenylamino radical in its line-width and overall spread, but had a different *g*-value. The mother liquor from the crystallization of the crude tetraphenylhydrazine also gave a similar spectrum. The mechanism for the formation of tetraphenylhydrazine is presumed to be the oxidation of diphenylamine into diphenylamino radicals, two of which combine to form a molecule of tetraphenylhydrazine. The species, whose spectrum we have observed, might be that of the diphenylamino radical further oxidized; the presence of three components may be indicative of this radical containing only one nitrogen atom.

III. Studies on Diphenylbenzidine.—1. Diphenylbenzidine behaved in a manner analogous to diphenylamine, when treated with acetic acid and PbO_2 (Fig. 7). The five-line resonance spectrum did not undergo any change when deuterated acetic acid, CH_3COOD, was used instead of CH_3COOH.

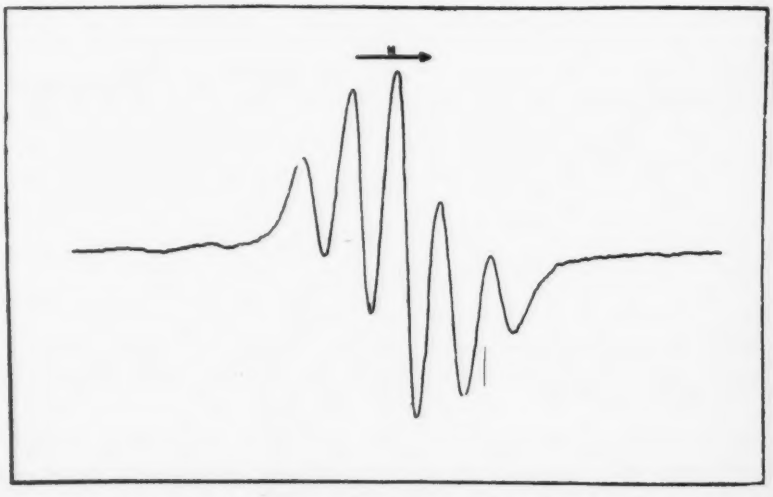


FIG. 7. Derivative of the electron spin resonance spectrum of a solution of diphenylbenzidine in acetic acid treated with PbO_2. The radical is the same as that in Figs. 2 and 5.

2. In a non-polar solvent like xylene, the oxidation of diphenylbenzidine with PbO_2 or AgO, resulted in an asymmetric paramagnetic resonance spectrum (Fig. 8). It is believed that more than one radical is formed and the measurement of *g*-value has no meaning due to the ambiguous nature of the spectrum. The spectrum could be interpreted as consisting of a less intense line superimposed on a stronger three-line spectrum. If this interpretation is correct the *g*-value of the 3-component species is 2·0030 ±0·0005.

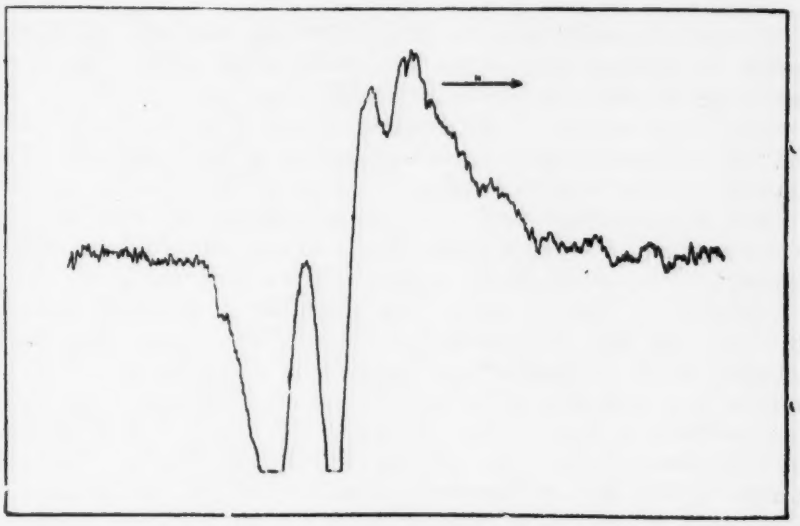


FIG. 8. Derivative of the electron spin resonance spectrum of a solution of diphenylbenzidine in xylene oxidized with PbO_2.

CHARACTERISTICS OF THE ELECTRON SPIN RESONANCE SPECTRA OF FREE RADICALS

The electron spin resonance spectra of organic free radicals are characterised by the *g*-values, the hyperfine structure and the separation between the hyperfine components, the line-widths of the components and the overall spreab of the spectra. Among these the *g*-values and the hyperfine structure are most useful in differentiating between radical species. The *g*-values of organic free radicals containing C, H, O and N have been found to cluster around the free electron value of 2·0023 and great precision in the determination of *g*-value is necessary for differentiating between organic free radicals only on the basis of their *g*-values. The almost

complete quenching of spin-orbit interaction in organic free radicals results in the isotropic part of the *g*-tensor (the part which is measured in solutions) being very close to the free electron value and the small deviations from the free electron value are presumably due to second order contributions from spin-orbit coupling.

The rich hyperfine structure usually observed in the electron spin resonance spectra of organic free radicals gives considerable information about the nature and structure of the free radical. It arises from the magnetic interaction of the electron magnetic moment with the magnetic moment of the nuclei, the magnitude of this interaction being reflected in the spacings between the hyperfine components. In solutions of low viscosity, the magnitude of the hyperfine interaction with a particular nucleus is directly proportional to the density of the unpaired electron at this nucleus,[18] and a study of the hyperfine pattern gives information on the distribution of the unpaired electron over the molecule. Most of the hyperfine structure observed in the radicals related to tetraphenylhydrazine has been attributed to interaction with nitrogen nuclei (except in the radical formed when a solution of tetraphenylhydrazine in acetic acid is treated with a drop or two of concentrated sulphuric acid). The magnitude of splittings measured are of the same order as those found for nitrogen splittings in other radicals (compare DPPH in benzene[19] or peroxylamine disulphonate ion[20]). The splittings due to protons in the phenyl rings of these radicals are usually very small and we have not observed them. The only proton splitting that has been observed in this study is due to the proton derived from the acidic medium, in the reaction between concentrated H_2SO_4 and tetraphenylhydrazine in an acetic acid medium; even here the proton is outside the phenyl ring.

The hyperfine structure spacings have been reported only for some of the radicals studied because of the large uncertainties involved in the overlap corrections when the individual components have line-widths comparable to the *hfs* separations. The hyperfine spacings in spectra, which are not sufficiently well resolved, are, therefore, less reliable criteria than the *g*-values for differentiation between radicals. In our investigation, we did not have to rely on *hfs* spacings for differentiation between radicals except in one instance, *viz.*, the radical derived by the oxidation of tetraphenylhydrazine with PbO_2 in an acetic acid medium. It has five components and its *g*-value agrees with those of the other five-line radicals observed in this series; the spectrum, however, is very broad and spread over a larger region. The uncorrected *hfs* spacing of 9·1 gauss found for this radical is very much

different from the average of 7 gauss for the other five-line spectra. If there is an appreciable overlap between the components due to the larger line-widths of the components in this particular medium, the corrected *hfs* spacing would increase; hence, we are led to believe that we have here a radical, different from the radical which gives the same *g*-value but different *hfs* spacings.

The line-widths and the overall spread of the spectra depend considerably on the concentration of the radicals and the nature of the medium in which the radical is obtained. Whereas the isotropic part of the *g*-tensor and *hfs* spacings of radicals in solutions of low viscosity depend only on intramolecular interactions and are hence independent of the medium, the line-widths and consequently the overall spread of the spectrum depend also on intermolecular interactions. The interaction of the radical with its neighbours (lattice) decides the spin-lattice relaxation time and hence the line-width of the individual components. The dipolar and the exchange interactions that govern the line shape and the line-widths are concentration dependent. (It should be pointed out that in very concentrated solutions the hyperfine structure might be completely lost due to the phenomenon of exchange narrowing.) In certain cases, the lifetime of the radical itself is made short by fast reactions in which the radical takes part and the line-width becomes dependent on the rate of this reaction, which in turn is controlled by the concentration of the radical and the other reactions.[21] For the reasons cited above, we have not relied on line-widths in making systematic differentiations between the radicals. The observed line-widths are a function of the amplitude of the magnetic field modulation and the overlap between the different components of the spectra. It was not always possible to operate at low field modulation amplitudes due to the low free radical concentration; in such cases the line-widths and *hfs* spacings have not been reported.

Conclusion

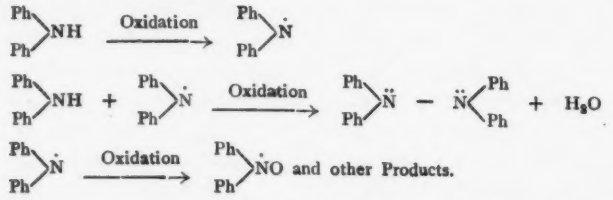
Tetraphenylhydrazine has been known, from the time it was first prepared, to undergo a variety of reactions involving free radical intermediates. We have attempted in our studies to provide positive proof for the formation of these radicals and to identify the reactions that may involve common intermediates.

1. Among the radicals which have 3-line spectra, we have identified the diphenylamino radical,

,

which is obtained either by heating a solution of tetraphenylhydrazine in xylene or by keeping the solution for a week or by bubbling oxygen through it.

2. The three-line spectrum obtained from diphenylamine, on oxidation with potassium permanganate [*See* Table I–II (2)] in an acetone medium cannot be attributed to the diphenylamino radical. The free radical results, perhaps, from the successive oxidation of the diphenylamino radical by excess potassium permanganate:



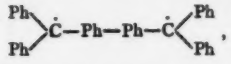
The spectrum reported by Hoskins for the radical obtained by passing oxygen through a hot solution of diphenylamine in a mixture of toluene and alkaline alcohol, and presumed to be diphenyl nitric oxide,

does not agree with our spectrum and the *g*-values are also different. The nature of the radical we have observed is, therefore, not well understood.

3. We believe that the asymmetric spectrum obtained by the oxidation of diphenylbenzidine with AgO or PbO_2 in a non-polar solvent [*see* Table I–III (2) and Fig. 8] is from more than a single radical species. The *g*-value of the major three-line radical does not agree with that of the diphenylamino radical, and the radical could either be Ph–Ṅ–Ph–Ph–NH–Ph, or the biradical, Ph–Ṅ– h–Ṅ–Ph, obtained by the oxidation of either one or both of the imino groups of diphenylbenzidine, Ph–NH–Ph–Ph–NH–Ph, respectively. The biradical is rather unlikely to be formed on account of the higher stability of the diamagnetic quinonoid compound,

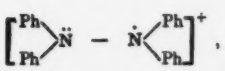
In this connection, it may be mentioned that the carbon analogue of this compound, Chichibabin's hydrocarbon,

is found to be diamagnetic. Hutchison and co-workers and also later workers have observed electron spin resonance from the solution of this hydrocarbon, corresponding to this hydrocarbon existing in the biradical form

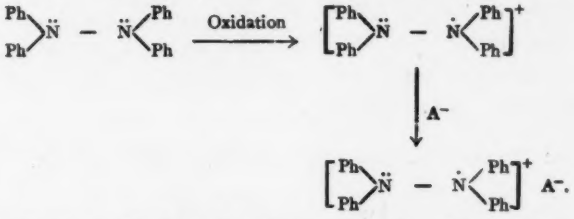


to about 4%.[22] Ingram, however, observes that the signal might have been due to an impurity.[23]

4. The radical,

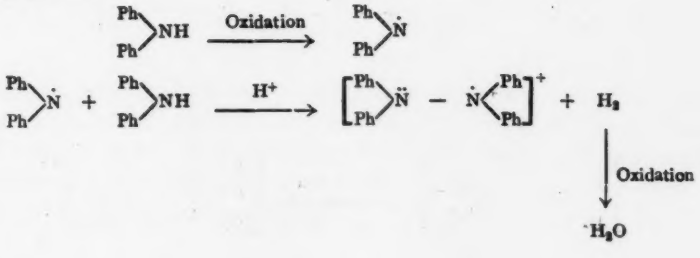


is formed under various conditions: (*a*) on heating a solution of tetraphenylhydrazine in acetic acid; (*b*) by the ageing of a solution of tetraphenylhydrazine in acetic acid; and (*c*) when diphenylamine or diphenylbenzidine is oxidized with PbO_2 in an acetic acid medium. Weitz and Schwecten have suggested that in acid solution this radical is formed by the removal of an electron from a molecule of tetraphenylhydrazine; the resulting cation can then form a salt with the anion of the acid.[2] A molecule of tetraphenylhydrazine itself can act as the oxidizing agent:

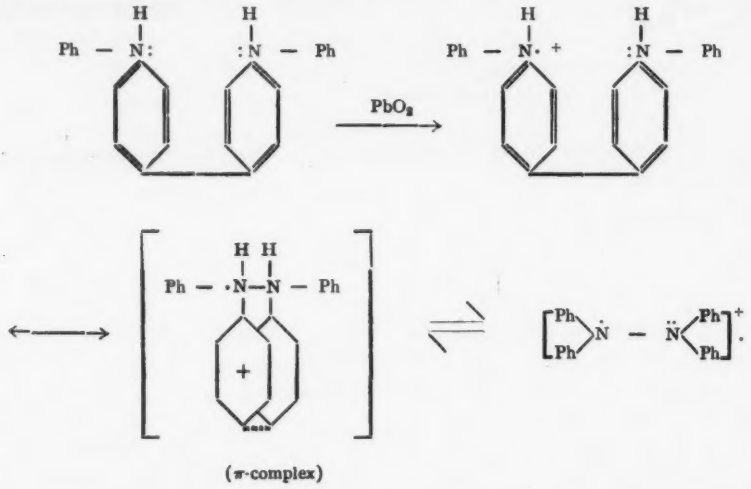


The formation of this radical on keeping an acetic acid solution of tetraphenylhydrazine is perhaps due to atmospheric oxidation. It is possible that the same radical is derived from diphenylamine and diphenylbenzidine in the following manner:

Diphenylamine:

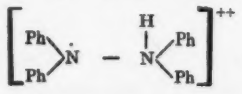


Diphenylbenzidine:

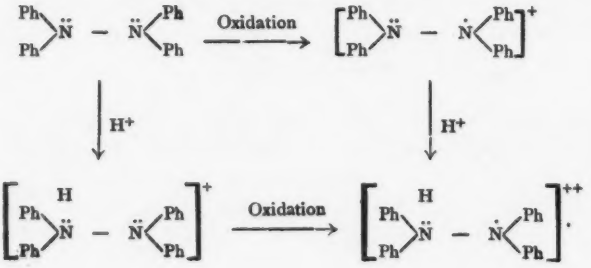


A similar π-complex is at present believed to be the transition state in the benzidine rearrangement.[24] The two aromatic rings fold on each other and the energy difference before and after the folding is extremely small; [24] and the formation of the tetraphenylhydrazinium radical is believed to be through a π-complex transition state and may be compared to the reverse of the benzidine rearrangement.

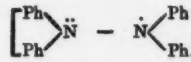
5. The protonated tetraphenylhydrazinium radical,



is obtained when a drop or two of concentrated sulphuric acid is added to a solution of tetraphenylhydrazine in acetic acid.

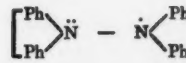


6. We have not understood the nature of the radical formed when tetraphenylhydrazine is reacted with PbO_2 in acetic acid (Fig. 3); the radical is different from



but the presence of a five-line structure indicates a >N–Ṅ< structure for this radical also.

7. On atmospheric oxidation of tetraphenylhydrazine in acetic acid, the radical formed as the initial step seems to be different from the tetraphenylhydrazinium radical,

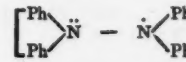


prolonged oxidation, however, leads to the formation of the tetraphenylhydrazinium radical. The nature of the radical formed as the first step is not well understood.

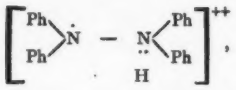
Summary

The free radicals obtained from tetraphenylhydrazine, diphenylbenzidine and diphenylamine under different conditions have been investigated with electron spin resonance techniques. The identification and differentiation between the radicals were done on the basis of their *g*-values and the line-widths and hyperfine structure exhibited by their spectra. The formation of the diphenylamino radical,

by the thermal dissociation of tetraphenylhydrazine in non-polar solvents has been confirmed. The same radical is obtained when tetraphenylhydrazine is subjected to atmospheric oxidation in a non-polar solvent. The tetraphenylhydrazinium radical ion,



is formed (1) when a solution of tetraphenyl-hydrazine in acetic acid is subjected to prolonged atmospheric oxidation, (2) when a similar, freshly prepared solution is heated and (3) when diphenylamine or diphenylbenzidine is subjected to oxidation in an acetic acid medium. It is believed that the protonated hydrazinium radical,



results if an acetic acid solution of tetraphenylhydrazine is treated with a few drops of concentrated sulphuric acid.

During the course of this investigation, the *g*-value of a 0·002 M solution of DPPH in xylene was measured to be 2·00347±0·00004.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. M. Vecera, Research Institute for Organic Syntheses, Pardubice-Rybitvi, Czechoslovakia, for initiating this problem and providing them with a sample of tetraphenylhydrazine on which the preliminary experiments were conducted. They also wish to thank Shri K. V. Lingam for help in obtaining the electron paramagnetic resonance spectra of some of the free radicals studied and Dr. S. S. Dharmatti for numerous helpful discussions.

REFERENCES

1. Wieland, H. .. *Ann.*, 1911, **381**, 212.
   ——— and Lecher, H. .. *Ibid.*, 1912, **392**, 156.
2. Weitz, E. and Schwecten, H. W. *Ber.*, 1927, **60**, 1203.
3. Lewis, G. N. and Bigeleison, J. *J. Am. Chem. Soc.*, 1942, **64**, 2808.
4. ——— and Lipkin, D. .. *Ibid.*, 1942, **64**, 2801.
5. Hoskins, R. .. *J. Chem. Phys.*, 1956, **25**, 788.
6. Wertz, J. E. .. *Chem. Revs.*, 1955, **55**, 922.
   Fraenkel, G. K. .. *Ann. N.Y. Acad. Sci.*, 1957, **67**, 553.
   ——— and Segal, B. .. *Ann. Rev. Phys. Chem.*, 1959, **10**, 435.
7. Knoebel, H. L. and Hahn, E. L. *Rev. Sci. Instr.*, 1951, **22**, 904.
8. Hewlett-Packard Application Note No. 2, *Frequency Measurement of Low-level Signals*, Hewlett-Packard Co., 275, Page Mill Road, Palo Alto, California, U.S.A.
9. Lindstrom, G. .. *Phys. Rev.*, 1951, **78**, 817; *Physica*, 1951, **17**, 412; *Arkiv. Fysik*, 1951, **4**, 1.
10. Driscoll, R. L. and Bender, P. L. *Phys. Rev. Letters*, 1958, **1**, 413.
11. Dumond, J. W. and Cohen, E. R. *Ibid.*, 1958, **1**, 291.
12. Ingram, D. J. E. .. *Free Radicals as Studied by Electron Spin Resonance*, Butterworths Scientific Publications, London, 1958, Chap. 5, p. 136.

13. Vecera, M. .. Research Institute for Organic Syntheses, Pardubice-Ribitvi, Czechoslovakia.

14. Weygand, C. .. *Organic Preparations*, Interscience Publishers, Inc., New York, N.Y., 1947, Chap. 5, p. 244.

15. Wieland, H. .. *Ber.*, 1913, **46**, 3300.

16. Roberts, J. D., Regan, C. M. and Allen, I. *J. Am. Chem. Soc.*, 1952, **74**, 3679.

17. Bailer, Jr. J. C. .. *Inorganic Syntheses*, McGraw-Hill Publishing Co., Ltd., New York, N.Y., 1954, **4**, 12.

18. Weissman, S. I. .. *J. Chem. Phys.*, 1954, **22**, 1378.

19. Hutchison, C. A., Pastor, R. C. and Kowalsky, A. G. *Ibid.*, 1952, **20**, 534.

20. Pake, G. E., Townsend, J. and Weissman, S. I. *Phys. Rev.*, 1952, **85**, 682.

21. Ward, R. L. and Weissman, S. I. *J. Am. Chem. Soc.*, 1954, **76**, 3612.

Gardner, D. M. and Fraenkel, G. K. *Ibid.*, 1956, **78**, 3279.

22. Hutchison, C. A., Kowalsky, A. G., Pastor, R. C. and Wheland, G. W. *J. Chem. Phys.*, 1952, **20**, 1485.

Jarret, H. S., Sloan, G. J. and Vaughan, W. R. *Ibid.*, 1956, **25**, 697.

23. *See* Reference 12, Chap. 8, p. 229.

24. Dewar, M. J. S. .. *Theoretical Organic Chemistry—The Kekulé Symposium*, Butterworths Scientific Publications, London, 1959, p. 199.

HELICAL CONFORMATIONS OF POLYPEPTIDE CHAINS

By V. Sasisekharan

(*Department of Physics, University of Madras, Madras-25*)

Received March 31, 1961

(Communicated by Dr. G. N. Ramachandran, F.A.Sc.)

1. Introduction

This paper deals with a study of the possible helical structures that can be built out of polypeptide chains, consistent with the demands of stereochemistry. The stereochemical restrictions in such structures may be divided into two types,

(*a*) those which demand that the bond distances and the bond angles between directly bonded atoms shall have specified values, and

(*b*) corresponding lengths and angles for secondary bonds, such as hydrogen bonds, shall lie within certain ranges, and similarly the contact distances between unbonded atoms shall not be less than certain limiting values.

In this paper, methods are developed whereby all possible simple helical structures satisfying the first condition (*a*) may be listed and described. It is assumed that the atoms in the peptide residue lie in a plane and that the configuration is that given by Corey and Pauling.[1] Once this is defined the only other restriction that enters the picture is the value of the 'tetrahedral' angle at the α carbon atom. This is so if the so-called R-group specifying the type of amino-acid residue is neglected. Thus, the attempt has been essentially to describe the single helices that can be built out of peptide residues neglecting secondary bond formation or steric hindrance. When the formation of hydrogen bonds is also taken into account it can be shown that the well-known α and γ helices of Pauling and others[2] come out. In fact, these are particular cases of slightly more general configurations. So also, it is found that the extended β structure and the pleated sheet structure of Pauling and Corey[3] are also only particular cases of a range of structures possible, in which every alternate residue has the same orientation (*i.e.*, digonal helices with two residues per turn). The method described here could also be utilised for finding out the co-ordinates of atoms when the elements of a helical structure are known from other data.

2. Description of the Helix

In an arrangement of polypeptide residues in a regular helix, it should be possible to bring any residue into another equivalent residue by a rotation about the helix axis accompanied by a translation along that axis. We shall indicate the values of these two for the operation of bringing a residue to its neighbour by a rotation ψ (which we shall call the unit twist) and a translation h. This operation, if repeated a number of times, would lead to a helical structure. The translation h is always taken to be positive (say along OZ) and so if ψ is $+$, *i.e.*, it is anti-clockwise looking from Z towards O, then it leads to a right-handed helix, and *vice versa*.

Since the peptide residue is a rigid planar structure, its position and orientation could be specified by the positions of the α carbon atoms at which they are linked to one another and the orientation of the plane of the residue with respect to some standard plane passing through successive α carbon atoms. Thus in Fig. 1 the group $C_1\ (H_1R_1)\cdot C_1'O_1 \cdot \cdot N_1H_1 \cdot C_2(H_2R_2)$ joining at C_2 with the next residue could be represented by the line C_1C_2 forming one of the links of a chain of rods arranged in a helical fashion. Neglecting first the orientation of the plane of the residue with respect to the line C_1C_2, we shall consider the parameters required for specifying the configuration of the helical chain consisting of equal rods, each of length L equal to C_1C_2. The points C_1, C_2, etc., occur on a continuous helix (the thin line of Fig. 1) which may be considered to be wound on a cylinder of radius R and having a pitch P. Its projection on the basal plane perpendicular to the axis of the helix will be a circle of radius R. The points C_1, C_2, etc., occur at regular intervals on the continuous helix and in the projection the straight lines $\bar{C}_1\bar{C}_2$, $\bar{C}_2\bar{C}_3$, etc., all subtend the same angle ψ at 0. Clearly the number of links per turn of the helix n is equal to $2\pi/\psi$. If μ is the tilt of the rods C_1C_2, etc., *i.e.*, the angle made with the horizontal, and h and l are its vertical and horizontal components, then the following relations are obtained:

(i) $h = L\sin\mu;\ l = L\cos\mu$

(ii) $l = 2R\sin\left(\frac{\psi}{2}\right)$

(iii) $h = \frac{P}{n}$.

The number n defined above need not be integral for a discontinuous helix, like the one we are considering. Thus, given the length L of the links,

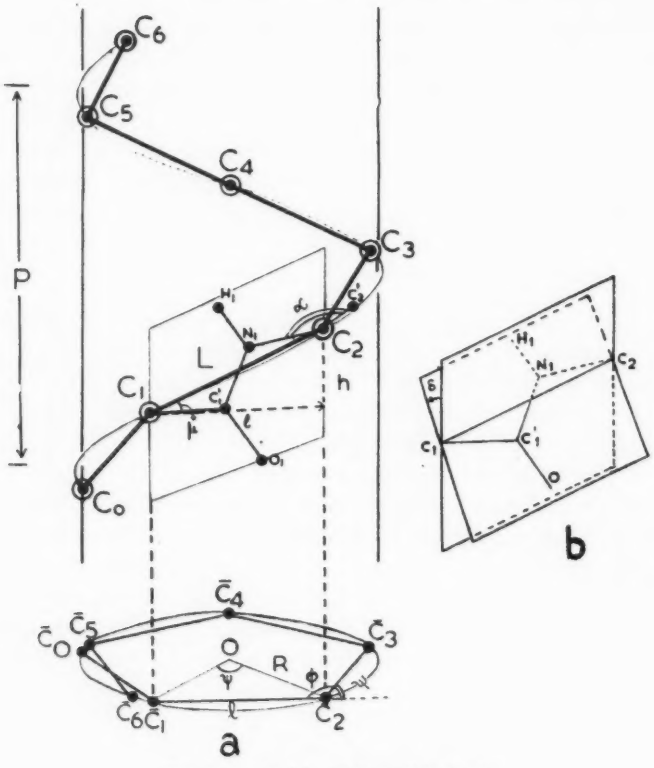


FIG. 1 *a* and 1 *b*. Polypeptide helix.

the helix requires two parameters for its specification. This could be, for instance, the pitch P and the radius R of the continuous helix associated with it *or* the tilt μ and the unit twist ψ, which is the same as the angle subtended by it at the centre in the projection, *or* the tilt μ and the number of links per turn n.

For discontinuous helices it is sufficient to consider the range 0 to π of the angle ψ, *i.e.*, the range ∞ to 2 of n. This so because if ψ happens to be greater than π, it will be less than π when measured in the opposite sense. Consequently, it will be equivalent to a discontinuous helix of the opposite sense but with ψ less than π. Therefore, all possible helices made up of links of a definite length, say L, can be covered by considering the range 0 to $\pi/2$ of the tilt μ and the range 0 to π of the unit twist ψ. The range 0 to $-\pi/2$

of the tilt only duplicates what is obtained in the range 0 to $\pi/2$. Reversing both μ and ψ leads only to the same configuration.

Considering now the full residue with its constituent atoms, further restrictions are brought in. Thus the angle at an α carbon atom, such as C_2, between the bonds N_1C_2 and C_2C_2' cannot be arbitrary but must be equal to the tetrahedral angle, which is denoted here by α. Consequently once the elements of the helix (μ, ψ) are fixed, the azimuth of the plane with respect to the line C_1C_2 cannot have an arbitrary value. We shall define this azimuth by the angle δ shown in Fig. 1 *b*, which is the angle by which the plane is rotated from a vertical position about the axis C_1C_2. The standard orientation is taken to be that in which the bond $C'O$ points downwards and δ is taken to be positive for anti-clockwise rotation looking from C_1 to C_2. Actually it is found that, given the values of μ and ψ, there are, in general, two orientations of the plane of the residue for which the angle α takes the required value. It may of course happen that for certain ranges of μ and ψ, the angle at the α carbon atom can never be made equal to the required value, so that such helices cannot occur for poplypeptide residues. When the two possibilities do occur for a definite (μ, ψ), these two are not equivalent and should, in fact, be considered as different possible structures. Consequently from the structural point of view the more important parameters are, μ the tilt and δ the azimuth of the plane of the residues. So also it is found more convenient to use the angle between the projection of two successive elements (for example, the angle $\bar{C}_1\hat{\bar{C}}_2\bar{C}_3$ in Fig. 1 *a*), rather than the angle ψ to specify the helix. The relation between these is $\phi = \pi - \psi$. Consequently $n = 2\pi\ (\pi - \phi)$. Hereafter we shall only use μ and ϕ to specify the discontinuous helix. The sign of ϕ is taken to be the same as that of ψ.

Now, if μ and δ are given, the elements of the helix (μ, ϕ) are not uniquely fixed. In fact, two helices can be constructed, one of which is right-handed and the other is left-handed. However, we shall restrict ourselves to helices of one hand, say all right-handed, *i.e.*, corresponding to ϕ positive. Then the complete range can be covered by considering the range 0 to $\pi/2$ of the tilt μ and the full range $-\pi$ to $+\pi$ of the azimuth δ. All other possibilities of μ, δ and ϕ are then either the duplicates of those contained in this range or only enantiomorphs of these, *i.e.*, left-handed helices. The relationship between these three parameters is shown in Fig. 2 which is a surface in three dimensions and whose equation is the relationship between μ, ϕ and δ. The diagram has been drawn corresponding to the calculations made by the author for some sections of the surface taking the angle at the α carbon atom (α)

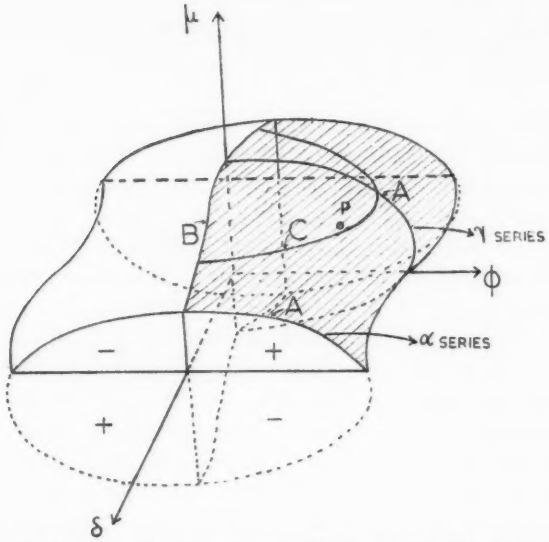


FIG. 2. A surface in three dimensions representing the relationship between the parameters δ, ϕ and μ of a helical structure.

to be 110°. It will be seen that the angle ϕ has an upper limit namely 119° so that n should be less than $360/61 \approx 6$. Consequently, all helices composed of amino-acid residues must have their number of residues per turn between 2 and 6. So also there is an upper limit 72° 30′ for the tilt μ. In this diagram only the shaded quarter need be considered for working out the full range of configurations. All the helices in this range are right-handed ones. If either ϕ or μ is made negative, we get left-handed helices. The relation between equivalent helices in the different ranges is shown in Table I. Here the symbol

TABLE I

Relation between equivalent helices

Sign of μ	Sign of ϕ	Relation to helices in the positive range of μ
+ve	+ve	$H_+(\lvert\mu\rvert, \delta)$
−ve	+ve	$H_-(\lvert\mu\rvert, \pi + \delta)$
+ve	−ve	$H_-(\lvert\mu\rvert, -\delta)$
−ve	−ve	$H_+(\lvert\mu\rvert, \pi - \delta)$

$H(\mu, \delta)$ is used to denote a helix having the values μ and δ for tilt and azimuth, these two parameters occurring in the quarter shaded in Fig. 2. Since the helix is right-handed, *i.e.*, positive, it is denoted by $H_+(\mu, \delta)$. The symbol $H_-(\mu, \delta)$ would mean that the co-ordinates of the atoms are the same, but they refer to a left-handed co-ordinate system, *i.e.*, it is a left-handed helix, which is the enantiomorph of $H_+(\mu, \delta)$.

In what we have discussed above, the residue itself has been considered to be a planar structure without asymmetry. Thus the orientation of the remaining two groups H and R at the α carbon atoms is left unspecified. Both the configurations which are usually denoted by L and D could occur and they would obviously correspond to different structures, although μ, δ and ϕ are the same. To distinguish between these, we shall add another suffix L or D to the notation for the helix. Thus for a given μ and δ there are two right-handed helices $H_{L+}(\mu, \delta)$ and $H_{D+}(\mu, \delta)$ and two left-handed helices $H_{L-}(\mu, \delta)$ and $H_{D-}(\mu, \delta)$. It is obivous that $H_{D-}(\mu, \delta)$ is the enantiomorph of $H_{L+}(\mu, \delta)$ and correspondingly $H_{D+}(\mu, \delta)$ is the enantiomorph of $H_{L-}(\mu, \delta)$.

3. Possible Helices Satisfying the First Condition (*a*)

In Fig. 3 the dimensions of the backbone of a single residue ($-C_1 \cdot C_1'O_1 \cdot N_1H_1 \cdot C_2-$) have been drawn to scale for the co-ordinates

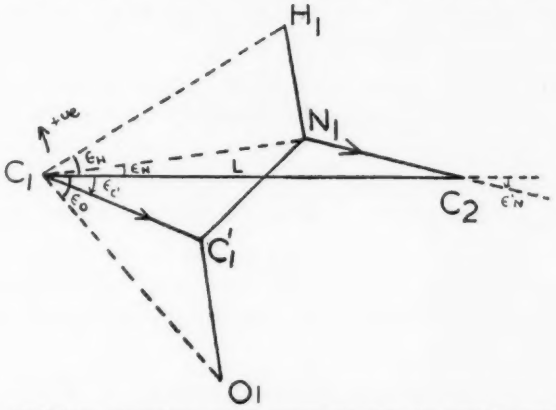


Fig. 3. Definition of various angles connected with the peptide residue.

given by Corey and Pauling[1]. The directly bonded atoms are jointed by lines. We are interested in the distances of the various atoms in the residue from the α carbon atom C_1 and angles between the lines joining them to C_1 and the line C_1C_2. These are marked in Fig. 3 and their values are given in Table II

TABLE II

Distances of the various atoms in the peptide residue (Fig. 3) from C_1 and the angle made by these lines with the line C_1C_2

Sl. No.	Atoms	Lengths	Angles
1	C_1C_2	3·79 Å	..
2	C_1C_1'	1·53 Å	$\epsilon_{C'} = 22°$
3	C_1O_1	2·41 Å	$\epsilon_O = 48° 15'$
4	C_1N_1	2·39 Å	$\epsilon_N = 8°$
5	C_1H_1	2·55 Å	$\epsilon_H = 31° 15'$
6	C_2N_1	1·47 Å	$\epsilon_N' = 13°$

(The angle ϵ is taken to be positive if measured in the anti-clockwise direction from C_1C_2.)

It would, of course, be useful if the full range of μ and δ were covered in working out the co-ordinates of the various helices H (μ, δ). However, this would be a laborious task, and therefore only certain sections of the surface in Fig. 2 have been worked out in full in this paper, and in doing so, the requisite techniques of calculation have been developed. The three types of sections studied are:

(*A*) δ = constant, = 0 or 180°, which corresponds to the types of helices worked out by Pauling and others[2] and includes the α, γ and π helices;

(*B*) ϕ = a constant, = 0°, which corresponds to the digonal helical structures. They have a two-fold screw axis of symmetry. Particular cases are the extended and the pleated sheet configuration of Pauling and Corey;[3] and

(*C*) μ = a constant, = 50°. This value was chosen, as this corresponds to a residue repeat of 2·90 Å, close to the residue repeats of collagen and polyglycine II.

These three ranges studied are marked as the *A*, *B* and *C* series in Fig. 2.

4. CYCLOGRAPHIC PROJECTION APPLIED TO THE PRESENT PROBLEM

In making the calculations, the cyclographic projection was found to be very useful. This projection is closely related to the stereographic projec-

tion. In a stereographic projection, a crystal face is represented by its pole (*i.e.*, the point at which the normal to the face intersects the unit sphere). In the cyclographic projection, on the other hand, it would be represented by the trace of the great circle, parallel to the crystal face (*i.e.*) by the great circle at right angles to the stereographic pole. Since a face is now represented by a great circle, the method is specially applicable to problems in which it is necessary to reproduce in projection, lines drawn on the crystal face. These would now be represented by points occurring on the great circle.

More generally, we may represent any plane (*e.g.*, the plane of the peptide residue) by a great circle and the orientation of the lines drawn in this plane (such as the lines C_1O_1, ..., C_1H_1 and C_2N_1) could then be represented by points on this great circle, the angular distance between representative points along the great circle in the cyclogram being equal to the angle between the corresponding lines on the plane.

In this study the axis of the helix is taken perpendicular to the plane of projection. If μ is known, the direction C_1C_2 is fixed, while the plane of the peptide is a great circle passing through this point. The previous residue is obtained by rotating the whole configuration through an angle $-\psi$ about the centre (*e.g.*, C_0C_1 of Fig. 4). For different values of ψ, it is possible to

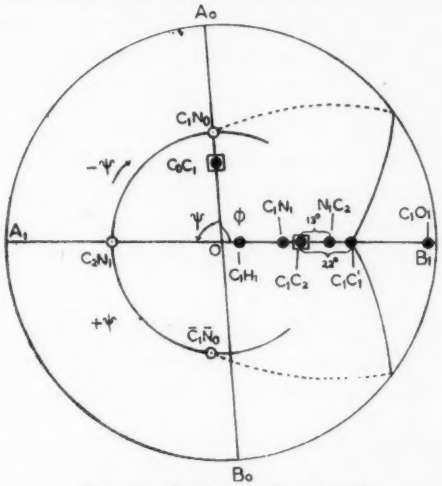


FIG. 4. Cyclogram for $\delta = 0°$.

read off the angle between the bonds N_0C_1 and C_1C_1' which should be equal to the tetrahedral angle α. Constructions were made with a 30 cm. Wulff net. Angles could be measured accurate to a quarter of a degree.

5. RESULTS

Configurations with Peptide Plane Parallel to the Helical Axis (Series A with $\delta = 0$ and 180°)

(*a*) *Determination of ϕ for various tilts.*—Here $\delta = 0°$ corresponds to the C = O group pointing down and $\delta = 180°$ to the group pointing up. Taking the first series, measurements were started with C_1C_2 horizontal; which was then tilted up at intervals of 5° and measurements were made for each tilt. Figure 4 is the cyclogram of a typical case with $\mu = 50°$. The directions of all the lines (C_1N_1, C_1C_1' ...) in the first residue would now occur on the meridian through C_1C_2 represented by the horizontal line A_1B_1 in the stereogram. In particular, the bonds N_1C_2 and C_1C_1' occur at latitudes $\mu - \epsilon_{N'} = \mu - 13°$ and $\mu - \epsilon_{C'} = \mu - 22°$ on this line. Considering the residue C_0C_1 previous to C_1C_2, its plane would be represented by another meridian A_0B_0 at an angle $-\psi$ to A_1B_1. We are interested in the "tetrahedral" angle between C_1N_0 and C_1C_1' and this angle should be equal to 110°. C_1N_0 can be obtained from the corresponding bond C_2N_1 (which is in the direction exactly opposite to N_1C_2) in the first residue, by rotating it through an angle $-\psi$. Thus the method of fixing ψ (or ϕ) is as follows. A circle is drawn with O as centre and radius equal to the distance C_2N_1 from O and the angular distance (along a great circular arc) of the various points on it from C_1C_1' is measured. That point for which this is equal to α gives the orientation A_0B_0 of the previous residue. It is obvious that there will be two settings C_1N_0 and $\bar{C}_1\bar{N}_0$ symmetrically situated with respect to the plane A_1B_1 for which the angle α is equal to the required value. These correspond to right-handed and left-handed helices respectively. Since we shall be dealing exclusively with right-handed helices for which ψ is positive or anti-clockwise, only the setting C_1N_0 which is to the left of C_1C_2 need be considered.

Thus for different values of μ the plane A_0B_0 is determined and the angle between A_1B_1 and A_0B_0 (*i.e.*, the angle $B_1\hat{O}A_0$) is measured. This gives $\phi = \pi - \psi$, and hence the number of residues per turn $n = 2\pi/\pi - \phi$.

This process was carried out, starting from $\mu = 0°$ and increasing the tilt until $\phi = 0°$, *i.e.*, $n = 2$. A value of 110° was first taken for the "tetrahedral" angle and for this angle the maximum possible value of μ was $72\frac{1}{2}°$. The same procedure was repeated with two other values of α, *viz.*, 105° and 115°. The relation between the tilt μ and angle ϕ is shown graphically in the three upper curves of Fig. 5 corresponding to the three values of α. Similar measurements were also made with the peptide turned through 180°, *i.e.*,

with C = O pointing up. But they were made only for $\alpha = 110°$. The data thus obtained are shown in the lower curve of Fig. 5.

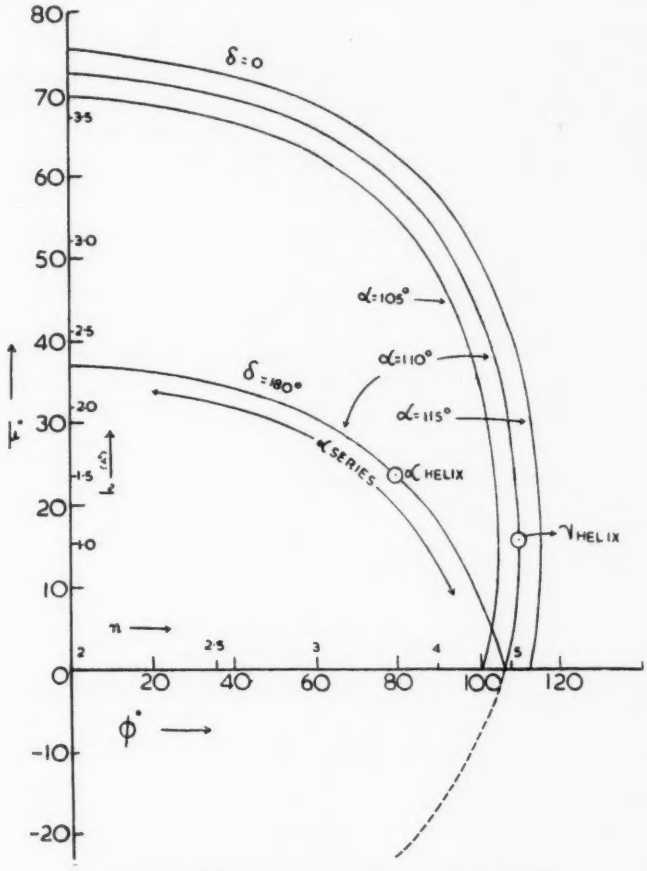


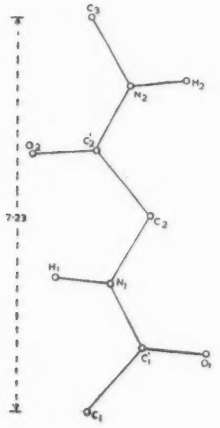
FIG. 5. Variation of ϕ with μ for $\delta = 0$ and 180°.

Along the co-ordinates of Fig. 5 are also marked n, the number of residues per turn, and h, the vertical height of the residue.

(*b*) *Discussion of the curves.*—It will be noticed from Fig. 5 that the turn ratio n for the same value of the tilt depends on the bond angle at the α carbon atom. In general, n decreases as α is decreased. The three curves for values of α changing by 5° are seen to be closely similar, the separation between any

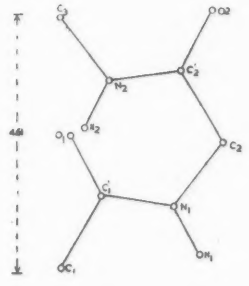
two being practically a constant. It is because of this that for the second range, calculations were made only for one value of α. In fact, for all the results described in the succeeding sections, only one value of α, *viz.*, 110° was used.

It will be noticed that for both $\delta = 0°$ and 180°, the maximum tilt occurs when $\phi = 0°$, *i.e.*, $n = 2$. In the first case this maximum value of μ is $72\frac{1}{2}°$ while for the second case it is only $37\frac{1}{2}°$. The former corresponds to the fully extended β-structure with a length of 7·23 Å for two residues and the atomic positions are drawn to scale in Fig. 6 *a*. The latter may be obtained



a

FIG. 6 *a*. Fully extended β structure.



b

FIG. 6 *b*. Bent β structure.

from this by rotating both the residues at the α carbon atom through 180°. This is a highly bent structure (Fig. 6 *b*) with a repeat of only 4·61 Å for two residues. It has very short contacts between atoms in the neighbouring residues and is therefore not possible for an actual structure. The entire range of configurations for $n = 2$ lies betwen $\mu = 37\frac{1}{2}°$ to $72\frac{1}{2}°$. In the next section the stereochemically possible ranges and the co-ordinates of the atoms for this type of digonal structure will be discussed.

The maximum possible value for ϕ when $\delta = 0°$ or 180° is α, the "tetrahedral" angle. Therefore ψ minimum is 70° and the maximum possible number of residues per turn is $n_{max.} = 5·14$. The lower curve for $\delta = 180°$ does not really have a maximum value, for it could be considered as a continuation of the upper curve for negative values of μ.

It is likely that actual structures do not take up all the configurations contained in the two curves in Fig. 5. We shall on the other hand consider which of these would be favoured if the condition that a hydrogen bond of length about 2·75 Å should be formed between NH and CO groups. The range is then considerably reduced.

Considering first the curve for $\delta = 180°$, the configurations in this case are all closely similar to the α helix. The α helix itself has a value 3·6 for n with $\alpha = 110°$ and has a practically straight hydrogen bond with the N—H . . . O length equal to 2·75 Å. However, if a slight variation in the "tetrahedral" angle from 105° to 115° is allowed and a short range in the neighbourhood of 2·75 Å for the hydrogen bond length is also permitted, then the range $n = 2$ to 4·4 of the lower curve can be utilised to form a helical structure in which a residue is hydrogen-bonded to its 1st, 2nd, 3rd, or 4th neighbour. The helices with $n = 4·3$ and 4·4 have been described, and are known as π-helices.[4] Other helices in the neighbourhood of $n = 2·2$ and 3·0 have also been described by Donohue,[5] who has also compared the stability of these helices.

Considering the upper curve ($\delta = 0°$), the γ helix of Pauling and others[2] belongs to this range with $n = 5·14$. Since n is nearly 5 for most of the region in the curve ($\delta = 0°$), it is not possible to have other helices of this type with an internal hydrogen bond and this is the only possible helix with probably a small possible change in n by varying the "tetrahedral angle' α. By the time n approaches 4, the pitch of the helix is larger than 12 Å and so no hydrogen bonds can be formed.

It may be mentioned that the discussion here is restricted to configurations with $\delta = 0°$ or 180° (*i.e.*, with the peptide plane exactly vertical). There is no stereochemical reason why this should be so, and if this restriction is removed, it may perhaps be possible to have hydrogen-bonded helical structures over a wider range of values of n than what has been stated above. This aspect has not yet been fully studied.

(*c*) *Derivation of the co-ordinates.*—Once the elements of the helix μ and ϕ are known, it is only necessary to know the co-ordinates of the atoms in any one residue to completely specify the structure. The position of any atom, *e.g.*, N is given in terms of its cylindrical polar co-ordinates r_N, θ_N and z_N with *OZ* as z axis and *OC* as the initial position in the perpendicular basal plane (Fig. 7), where C is the corresponding α carbon atom (*e.g.*, C_1 for the residue C_1C_2). Figure 7 is actually drawn for a general orientation of the peptide (δ other than 0° or 180°). When $\delta = 0°$ or 180° all the atoms

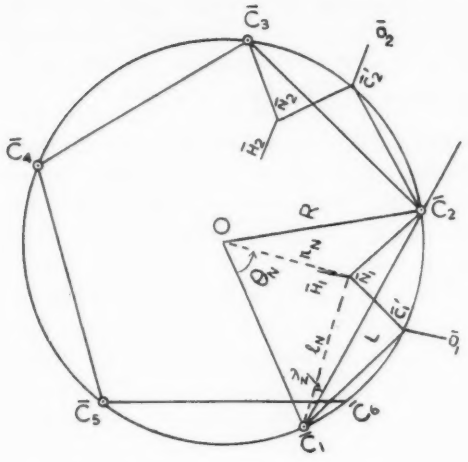


FIG. 7. Basal projection of polypeptide helix.

will lie in the projection on the line $\bar{C}_1\bar{C}_2$ (projected line of C_1C_2). The letters with bars over them indicate the positions of the atoms in the projection. If l_N ($= \bar{C}_1\bar{N}_1$) is the projected length of C N in the basal plane for a particular μ, then

$$l_N = L_N \cos(\mu + \epsilon_N) = L_N \cos \mu_N$$

where $\mu_N = \epsilon_N + \mu$ and L_N is the actual distance between C_1 and N_1 in the peptide plane, given in Table II. The three cylindrical co-ordinates can then be obtained in terms of R, the radius of the cylinder on which the α carbon atoms lie, l_N the projected length of C_1N_1 and L, the projected length of C_1C_2. Thus r_N is given by

$$r_N = \sqrt{l_N^2 + R^2 - l_N.l.}$$

The angle θ_N measured from $O\bar{C}_1$ in the projection is given by

$$\theta_N = \sin^{-1}\left[\frac{l_N \sin\frac{\phi}{2}}{r_N}\right].$$

The height z_N is given by

$$z_N = L_N \sin \mu_N.$$

Similarly the co-ordinates of the other atoms can be obtained. The values of r, θ and z for all the atoms in the peptide residue are plotted in Figs. 8 (*a* and *b*) against the tilt for a range covered by the curve for $\delta = 180°$. They correspond to the α series of helices with the range 4·5 to 2 for n.

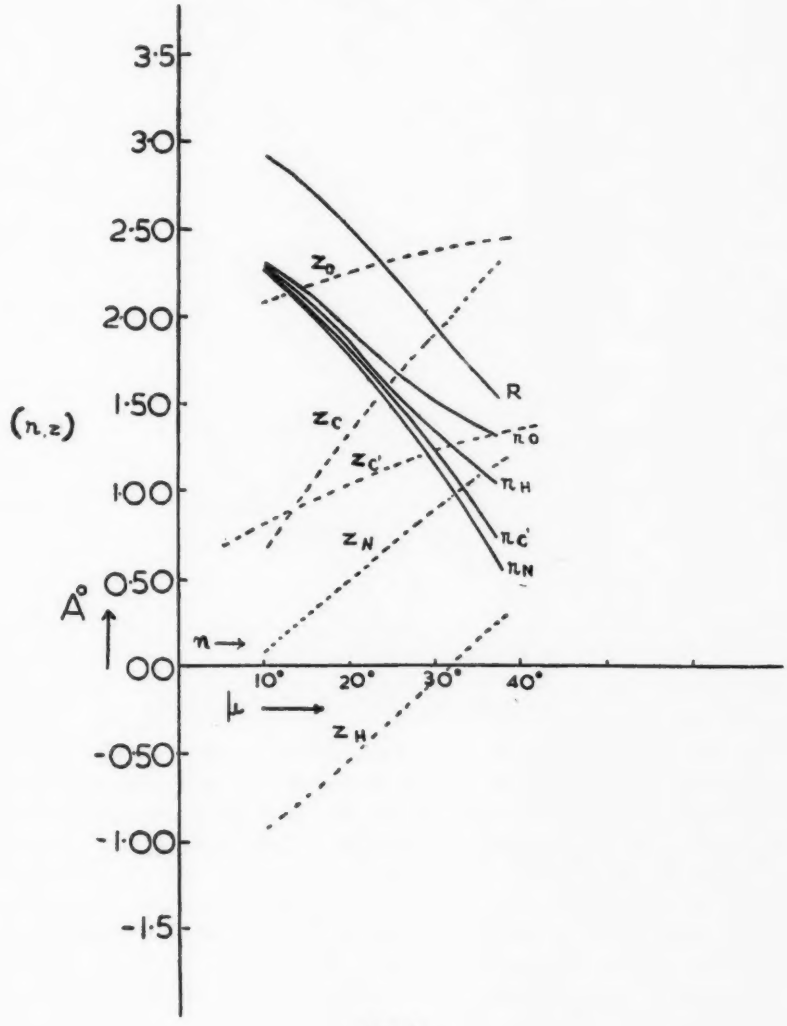


FIG. 8 *a*

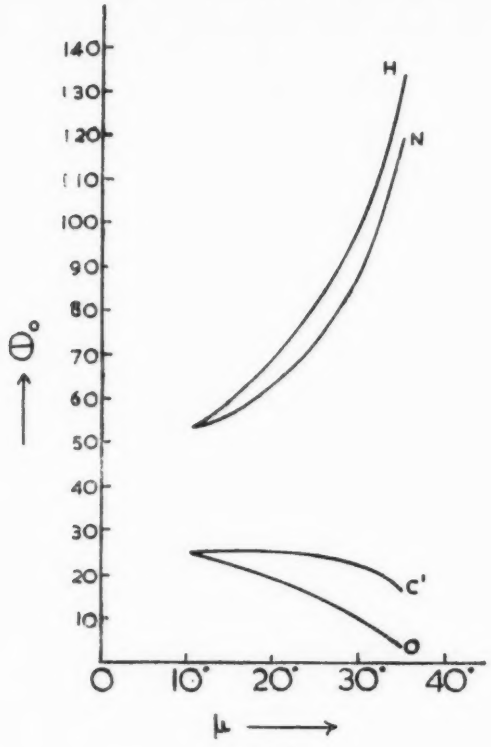


FIG. 8 *b*

FIGS. 8 *a* and *b*. Variation of r, θ and z with μ for the α series.

6. CONFIGURATIONS FOR $n = 2$; β STRUCTURES

(*a*) *Determination of* δ *for various tilts.*—For $\phi = 0°$, *i.e.*, $n = 2$, it has been pointed out in the previous section, that the tilt ranges from $\mu = 37\frac{1}{2}°$ to $72\frac{1}{2}°$. Over this range the azimuth δ would continuously change from 180° to 0°. Corresponding to a tilt μ, there will be a definite value of δ which can be determined as follows:

Corresponding to a particular value of μ, the pole of the peptide residue is on the great circle ***AB*** of Fig. 9, the angle δ being measured from the point ***A***. The line C_1C_2 is represented by the point C_1C_2. For the different azimuths the two directions C_1C_1' and N_1C_2 would lie on small circles with C_1C_2 as pole and radii equal to $\epsilon_{C'}$ and ϵ'_N. For $\delta = 0°$ they lie on the meridian through C_1C_2. For a value of $\delta = 60°$ (say), the pole of the peptide plane

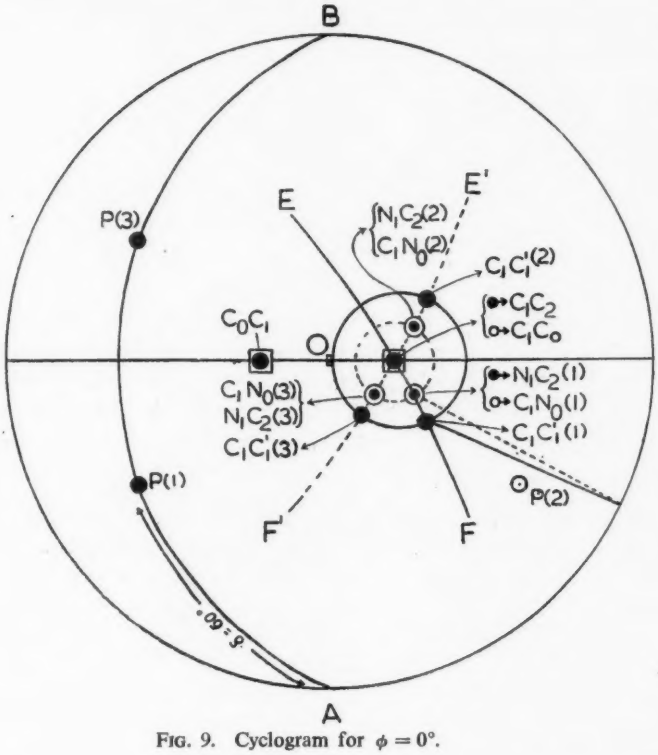


FIG. 9. Cyclogram for $\phi = 0°$.

is represented by P (l) in Fig. 9. The great circle corresponding to the peptide plane is EF whose pole is P (l) and the lines C_1C_1' and N_1C_2 are now represented by points on this great circle, and are marked as C_1C_1' (l) and N_1C_2 (1). Since we have definitely assumed that $\phi = 0°$ (or $\psi = 180°$) the previous residue would have its pole C_0C_1 on the same meridian as C_1C_2 but on the opposite side. Therefore C_1C_0 would occur at the same point as C_1C_2 but below the plane of the paper. Consequently the direction C_1N_0 will also lie on the dotted circle shown in Fig. 9 with C_1C_2 as pole, and it would coincide with N_1C_2, but would lie below the plane of the paper.

The problem is to determine the value of δ for which the angle between C_1N_0 (1) and C_1C_1' (1) is equal to 110°. As δ is varied, the angle between C_1N_0 and C_1C_1' will change and for the particular example shown in the diagram (*i.e.*, for $\mu = 67°$), the angle is 110° when $\delta = 60°$, as indicated.

More generally, for each value of μ, the position of the pole of the peptide on the great circle is determined for which C_1C_1' and C_1N_0 (which correspond to the intersection of the corresponding peptide plane with the two small cles) are at an angle of 110°.

If P is taken at $-\delta$, which is equivalent to choosing the pole P (2), the relevant directions in the plane are now represented by C_1C_2 (2), N_1C_2 (2), C_1N_0 (2) in the great circle $E'F'$.

Once again it will be seen that the angle between C_1C_1' (2) and C_1N_0 (2) will be the same as the angle between C_1C_1' (1) and C_1N_0 (1), considered earlier. Since $\phi = 0°$ or $\psi = 180°$, this is not a different helix, but may be seen to be equivalent to the former one, but going in the opposite direction. However, this second great circle has its other pole at P (3) which is opposite to P (2). Corresponding to this, the bond directions C_1C_1' and C_1N_0 occur at C_1C_1' (3) and C_1N_0 (3), and the angle between them is not the same as that between C_1C_1' (1) and C_1N_0 (1). This shows that δ and $180 - \delta$ are not equivalent, although $+\delta$ and $-\delta$ are. Hence, the whole range 0° to 180° of δ will have to be studied.

The above method was used to determine the values of δ corresponding to various values of the tilt μ. The graph connecting δ and μ is shown in Fig. 10.

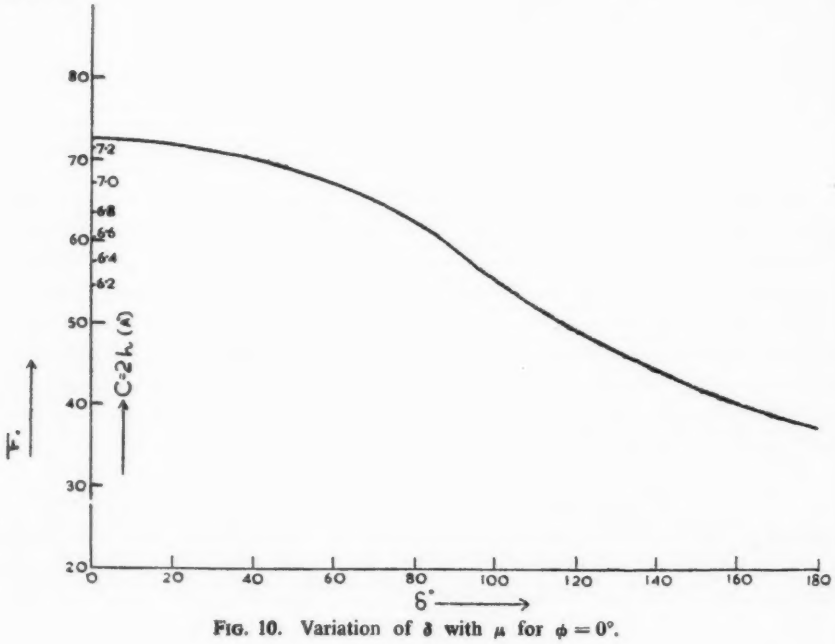


FIG. 10. Variation of δ with μ for $\phi = 0°$.

(*b*) *Discussion of the β structures.*—As already pointed out in the previous section, the polypeptide chain is fully extended when $\mu = 72\frac{1}{2}°$ (for $\delta = 0°$) and is buckled when $\mu = 37\frac{1}{2}°$ (for $\delta = 180°$). The latter position is obviously impossible (Fig. 6 *b*). The fully extended chain is quite satisfactory so long as only a single chain is considered. But if hydrogen bonds of the type N—H...OC have to be formed between chains arranged side by side, then if the chains are all parallel, the bonds cannot be straight, the angle between NH and NO being more than 30°. Even then only glycine can be accommodated in the side-chain. On the other hand if alternate chains go in opposite directions, as in the so-called anti-parallel structure, then good hydrogen bonds can be formed, but there are short contacts between the α carbon atoms if δ has a value 0°, *i.e.*, the chains are completely flat. If the chains are allowed to buckle slightly (δ is allowed to have values in the range 0° to 90°), hydrogen bonds can be formed between either parallel or anti-parallel chains. Thus for example, when $\delta = 67°$ (or $h = 3{\cdot}5$ Å) for polyglycine, there is no steric hindrance between parallel or anti-parallel chains and good hydrogen bonds can be formed in both cases with anti-parallel chains giving a more linear hydrogen bond.

Thus the steric hindrance between the side-chains may be relieved by allowing the chains to buckle according to the size and chemical nature of the side-chains and an appreciable range of repeat distances can be obtained with acceptable hydrogen bond configuration for both parallel and anti-parallel chain configurations. Actually this range of repeat distances was found to be $c = 6{\cdot}25$ to $7{\cdot}00$ Å for both the parallel and anti-parallel arrangements. These may be defined as the β type of structures. The corresponding change in μ is from 55° to 67° and in δ from 60° to 100°.

The ideal pleated sheet configuration described by Pauling and Corey[3] corresponds to $\delta = 90°$ and $c = 6{\cdot}5$ Å. The other pleated sheet configuration described by them is $c = 7{\cdot}0$ Å for $\delta = 60°$.

(*c*) *Derivation of the co-ordinates.*—In each case the positions of the poles C_1O_1, C_1C_1', etc., were noted. These could be obtained by drawing small circles corresponding to ϵ_0, $\epsilon_{C'}$, etc., about C_1C_2. The inclinations (μ_0, $\mu_{C'}$, etc.) of the lines C_1O_1, C_1C_1', etc., to the basal plane could be directly read off from the net. Thus for example if μ_N is the inclination of C_1N_1, then the projected length of C_1N_1 on the basal plane is given by

$$\bar{C}_1\bar{N}_1 = l_N = L_N \cos \mu_N.$$

The height above the basal plane is given by

$$z_N = L_N \sin \mu_N.$$

The azimuthal angle between $\bar{C}_1\bar{N}_1$ and $\bar{C}_1\bar{C}_2$ (Fig. 7) can also be measured from the net and is denoted by λ_N. Similarly, these three quantities l, z and λ were obtained for the other atoms.

When $\phi = 0°$ ($n = 2$), the structure is a digonal helix and therefore it is convenient to obtain the positions of the atoms referred to a rectangular co-ordinate system. The z-axis is taken to be parallel to the axis of the helix and passing through $\bar{C}_1$. The x-axis is taken to be along $\bar{C}_1\bar{C}_2$. The y-axis is perpendicular to $\bar{C}_1\bar{C}_2$ at $\bar{C}_1$ such that x, y, z form a right-handed system. Then the rectangular co-ordinates of any atom (say N_1) are then given in terms of z_N, l_N and λ_N by $x_N = l_N \cos \lambda_N$, $y_N = l_N \sin \lambda_N$, $z_N = z_N$.

The x, y and z co-ordinates for the range from $\mu = 50°$ to $72\frac{1}{2}°$ are given in Fig. 11. The co-ordinates of the atoms of the backbone are given in Table III for some β structures. The hydrogen-bond lengths, angles and the stereochemically possible β structures, both for the parallel and anti-parallel arrangements, are being worked out and will be reported later.

7. CONFIGURATIONS FOR CONSTANT TILT AND VARYING δ

(*a*) *Determination of ϕ for various δ* ($\mu = 50°$).—In this case the peptide link C_1C_2 was maintained at $\mu = 50°$ and the peptide plane was rotated about C_1C_2 over a full range, *viz.*, $-180° \leqslant \delta \leqslant 180°$. The variation of the number of residues per turn n (or ϕ) with the azimuth δ of the peptide plane was calculated. The plane was initially kept parallel to the helical axis and then rotated about C_1C_2 both in the anti-clockwise ($+\delta$) and clockwise ($-\delta$) directions. For this particular value of μ, the magnitude of δ has an upper limit 117°. So, measurements were made for values of δ at intervals of 10° over the range $-117° < \delta < 117°$. As will be seen from Fig. 5, δ can have the full range $-180°$ to $+180°$ only for values of μ less than $37\frac{1}{2}°$. The method of obtaining the angle ϕ for given μ and δ is as follows:

With $\mu = 50°$, the pole of C_1C_2 is plotted first (Fig. 12). Small circles corresponding to the angular values of $\epsilon_{C'}$ and ϵ'_N can be drawn about the pole C_1C_2. For convenience, the small circle ϵ'_N is drawn about the pole opposite to C_1C_2 in Fig. 12. The locus of the pole of the peptide for various values of δ will be the great circle ***AB***. The great circle is divided into intervals of 10°. For each of these poles, the corresponding great circle of the peptide plane is traced. In each case the intersections of the small circles with the great circle of the peptide plane should give the points representing C_1C_1' and C_2N_1 for the azimuth δ of the peptide.

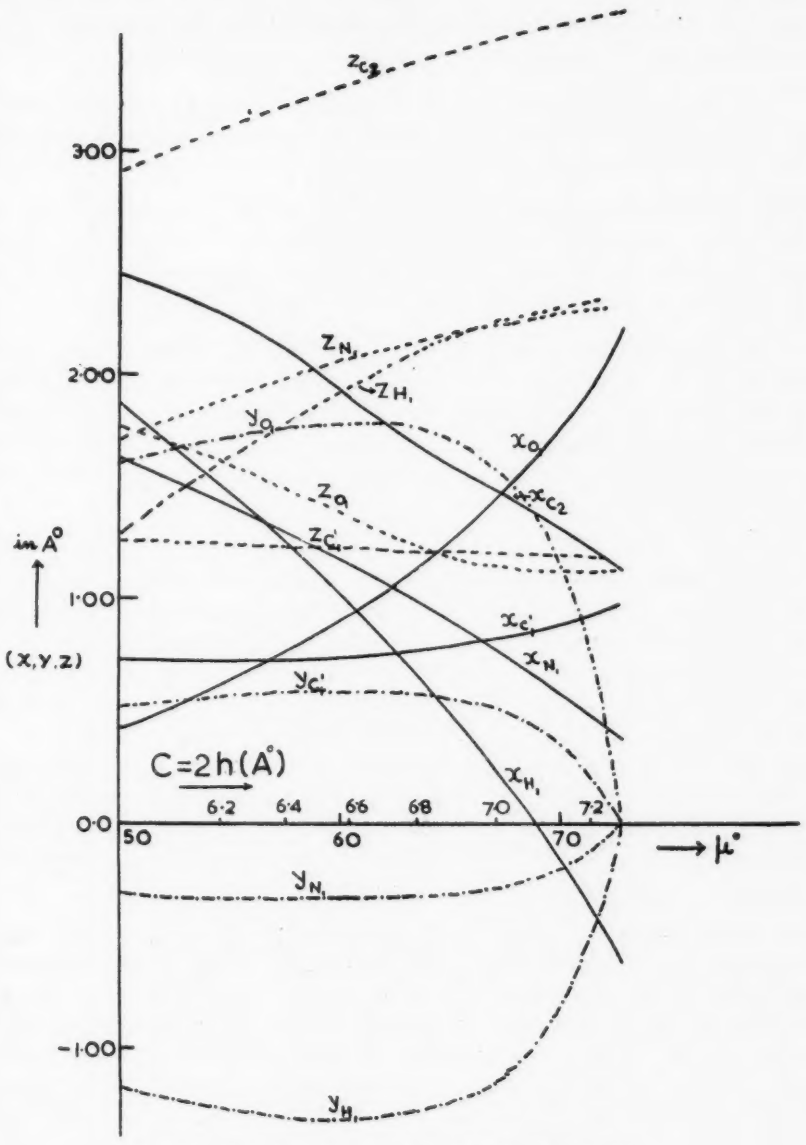


FIG. 11. Variation of x, y and z with μ for the β series.

TABLE III

Atomic co-ordinates for the backbone of some β structures
(These have been calculated from the value of c for an ideal structure)

(*a*) *Stretched pig bristle:* Fibre repeat $c = 6{\cdot}62$ Å ($\delta = 86°$)

Atom	x	y	z
C_1	0·00	0·00	0·00
C_1'	0·74	0·58	1·22
O_1	0·95	1·78	1·35
N_1	1·15	−0·35	2·06
H_1	0·95	−1·34	1·95
C_2	1·90	0·00	3·31

(*b*) *β-poly-γ-methyl-L-glutamate:* Fibre repeat $c = 6{\cdot}84$ Å ($\delta = 73°$)

Atom	x	y	z
C_1	0·00	0·00	0·00
C_1'	0·75	+0·55	1·20
O_1	1·125	+1·65	1·20
N_1	0·99	−0·35	2·15
H_1	0·65	−1·30	2·13
C_2	1·70	0·00	3·42

(*c*) *β-polyglycine:* Fibre repeat $c = 7{\cdot}00$ Å ($\delta = 60°$)

Atom	x	y	z
C_1	0·00	0·00	0·00
C_1'	0·82	0·50	1·20
O_1	1·46	1·58	1·15
N_1	0·77	−0·30	2·24
H_1	0·23	−1·15	2·24
C_2	1·49	0·00	3·50

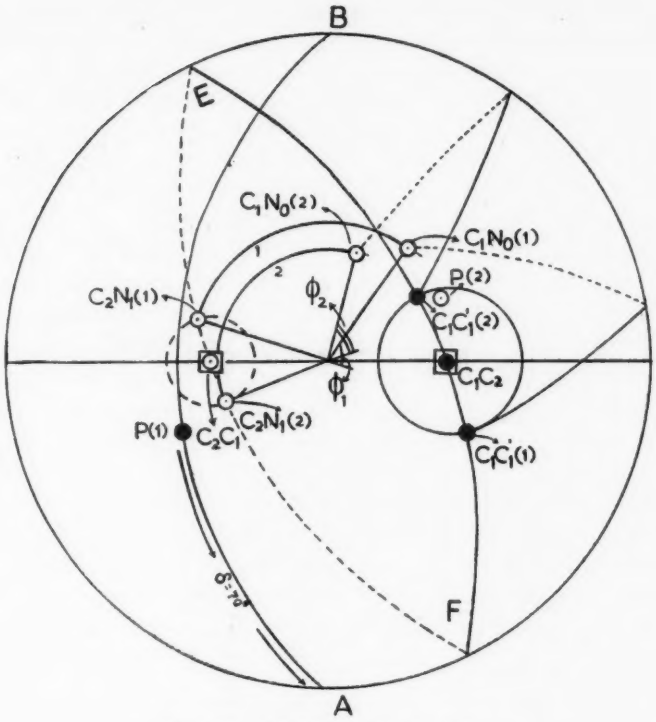


FIG. 12. Cyclogram for $\mu = 50°$.

As an example, let us consider the plane rotated through $\delta = 70°$ (Fig. 12) the pole being at *P*, 70° from *A*. The great circle representing the peptide plane for this pole *P* is *EF*. There are two sets of points C_1C_1' (1) C_2N_1 (1) and C_1C_1' (2) and C_2N_1 (2) given by the intersections of this great circle with the two small circles. These two sets correspond to the positions obtained by rotating the plane through δ (= 70°) and 180 + δ (= 250°) which is the same as taking $\delta = 70°$ in the anti-clockwise direction and $\delta = -110°$, *i.e.*, 110° in the clockwise direction. One is obtained from the other by turning the plane through 180° about C_1C_2. The corresponding pole of the peptide plane in the second position is *P* (2) at $\delta = -110°$.

The problem now is to find how much the previous residue C_0C_1 is to be rotated away from C_1C_2 so that the angle α becomes equal to 110°. As already pointed out, if the peptide planes should form a helical structure then the normals to these planes should make the same angle with the axis of the helix.

Therefore the plane C_0C_1 should also be rotated through $\delta = 70°$ or $-110°$ as the case may be from the vertical position.

Therefore C_1N_0 will lie on a small circle with O as centre and passing through the representative point of C_2N_1 as shown in Fig. 12, *i.e.*, it must lie on the small circle 1 for $\delta = 70°$ and on the small circle 2 for $\delta = -110°$. Now it is only necessary to find the points on these two small circles 1 and 2 which are at 110° from C_1C_1' (1) and C_1C_1' (2) respectively. These are marked in Fig. 12 and the values of ϕ in each case can also be directly read off on the Wulff net.

The above procedure was repeated for the whole range of δ and in each case the value of ϕ was noted. The graph connecting the azimuth δ with ϕ (and n) is shown in Fig. 13.

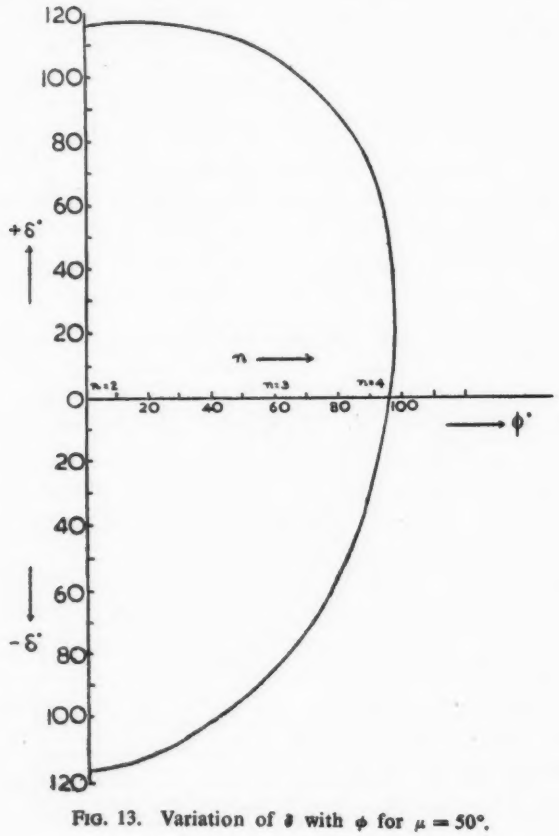


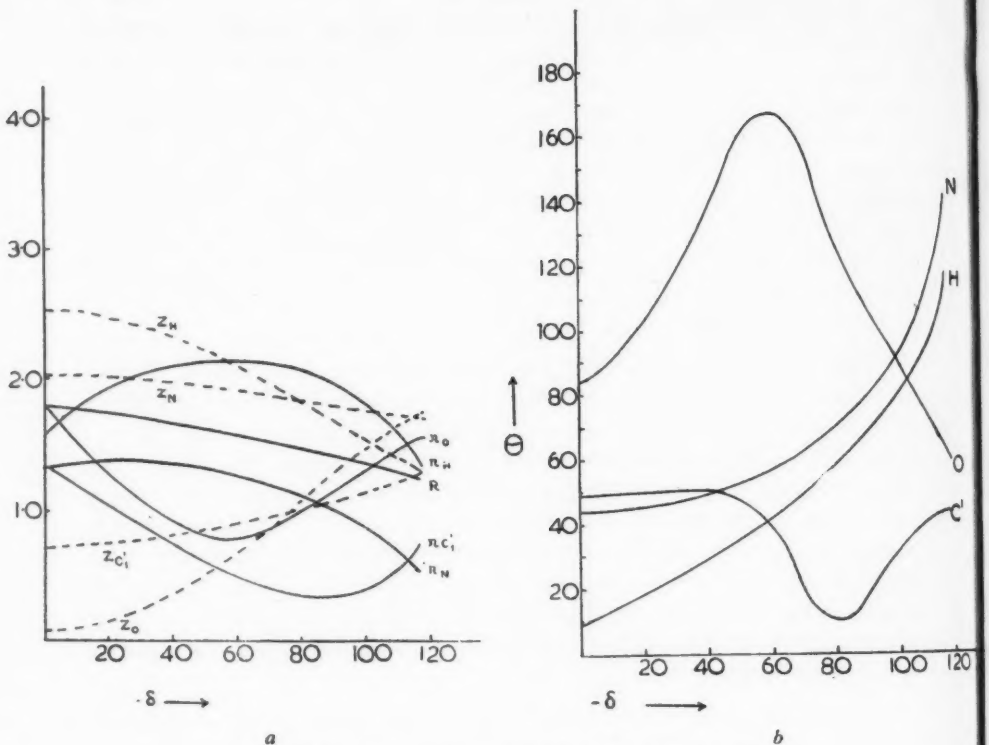
FIG. 13. Variation of δ with ϕ for $\mu = 50°$.

(*b*) *Discussion of the graph.*—The upper part corresponds to positive values of δ, *i.e.*, to anti-clockwise rotations of the peptide plane from the vertical standard position with C = O pointing down, whereas the lower part corresponds to clockwise rotations. In the helices corresponding to the upper part (δ positive) the C = O group points away from the axis of the helix, while in the case of helices with δ negative, the C = O groups point inwards towards the axis. Thus for a particular tilt μ, there are two helices with the same number of residue per turn corresponding to the clockwise and anti-clockwise rotations of the peptide with respect to C_1C_2, in one of which the CO groups are turned inwards, while in the other, the NH groups are pointing inwards.

This means that, in general, for a particular orientation of the peptide with respect to the helical axis there are two different helical configurations one with C′ atoms near the axis and the other with N atoms near the axis of the helix. These correspond to two values of δ separated by 180°. The two configurations mentioned by Crick and Rich[6] for polyglycine II, which correspond to $\mu = 54° 30'$ and $\delta = 90°$, have this type of relationship. If imino-acid residues like proline or hydroxyproline residues occur, the configurations with N atoms near the axis are not possible. The polypeptide chain configurations in poly-L-proline II,[7] poly-L-hydroxyproline A[8] and polyglycine II[6] are very similar and the point *P* marked in Fig. 2 is close to the above structures.

The maximum possible value of δ for a given value of μ is determined by the value of the angle α. In the present case where $\alpha = 110°$, the maximum value for $|\delta|$ is 117°. Because of this, it may not always be possible to have two structures in which the peptide is reversed with respect to each other, *e.g.*, in the above case of $\mu = 50°$, if $|\delta| < 60°$, the second corresponds to $|\delta| > 120°$ and is therefore not possible.

(*c*) *Derivation of the co-ordinates.*—For each value of δ, the positions of the points C_1O_1, C_1C_1', etc., were noted as in Sec. 6 (*c*) and the inclinations of the lines C_1O_1, C_1C_1', etc., were directly read off, on the Wulff net. As mentioned in Sec. 6 (*c*) the values of l, λ and z for each atom were also obtained. The absolute values of l, λ and z will be the same for both positive and negative values of δ. But in the projection the positions of the atoms in the two cases will be related by a reflection about a vertical plane through C_1C_2. The three cylindrical co-ordinates r, θ and z can then be obtained in terms of R (the radius of the cylinder on which the α carbon atoms lie) l, λ and z from equations similar to the ones given in Sec. 5 (*c*). As an example, the values of r, θ and z for all the atoms in the peptide residue are plotted in Figs. 14 (*a* and *b*)



FIGS. 14. *a* and *b*. Variation of r, θ and z with δ for $\mu = 50°$.

against the azimuth $-\delta$. These correspond to the series of helices in which the CO groups point inwards.

8. CONCLUSIONS

We have considered above methods whereby, when the tilt μ and one other variable (either δ or ϕ) is given, the remaining parameter can be determined. This method could be extended to cover the complete range of possible values for these quantities, but this is not reported here, since the attempt has been essentially to develop the methods for such a study. We have, however, obtained a knowledge of the nature of the relation between the three variables, *viz.*, the surface shown in Fig. 2. This corresponds to a value of 110° for α. For $\alpha = 105°$ and 115° two similar surfaces one within, and the other enclosing the surface for $\alpha = 110°$, will be obtained.

As was mentioned in the introduction, the attempt here has been mainly to list the possible configurations of single helices. Some ranges of these are immediately ruled out because of short contacts between atoms in the single chain itself. The next step is to consider the formation of stabilizing secondary bonds. These could be between residues within the chain itself or with other chains. Restricting ourselves to the former type, the bonds NH....OC (hydrogen bonds) may be nearly parallel to the helical axis or they may go across the centre of the helix and link with a group on the opposite side. A consideration of the former leads to the whole α series for which n may range from 2·2 to 4·4 and γ series with n near about 5. The latter seems to be impossible if only helices with every residue identical in its relation to the helical axis are considered for all the N—H's or all the C=O's will be pointing in, so that an N—H cannot link with a C = O across the axis of the helix. It will be worthwhile therefore to consider helices with a "helix repeat" of 2 residues. The particular case of such helices are the series of β structures, with residue repeat ranging from $c = 6{\cdot}25$ to $7{\cdot}00$ Å.

So also, if interchain bonds are considered with other than digonal structures, once again two classes arise, *viz.*, between helices wound on the same cylinder, that is with coincident axes, and helices with non-coincident axes. The former is not very difficult to work out and it appears that for polypeptides it is practically ruled out except perhaps for the extreme limit $n \approx 5$, $h \approx 2$ Å which is possible only if the tetrahedral angle is everywhere made about 115°. The latter would lead to coiled coil structures in general if n is non-integral. Some of these considerations are under study in this laboratory but they are beyond the scope of this paper.

The author wishes to express his grateful thanks to Prof. G. N. Ramachandran for the invaluable suggestions he gave during the course of this study. His thanks are also due to the Government of India, for the award of a research fellowship, during the tenure of which the work was carried out.

Summary

It is shown in this paper, how simple polypeptide helices for all possible orientations of the peptide residue with respect to the helical axis can be obtained by the method of cyclographic projection. The cyclographic projection is actually applied to three cases and the results are described. It is also shown that the celebrated α helix and the other helices, described so far, are particular cases of slightly more general ones. So also it is found that the extended β structure, and the pleated sheet structure of Pauling and Corey, are also particular cases of a range of structures possible, in which every

alternate residue has the same orientation (*i.e.*, digonal helices with two residues per turn). The method described here can also be used to find out the co-ordinates of atoms when the elements of a helical structure are known from other data.

REFERENCES

1. Corey, R. B. and Pauling, L. — "Fundamental dimensions of polypeptide chains," *Proc. Roy. Soc.*, 1953, **141 B,** 10.
2. Pauling, L., Corey, R. B. and Branson, H. R. — "The structure of proteins: Two hydrogen-bonded helical configurations of the polypeptide chain," *Proc. Nat. Acad. Sci.*, 1951, **37,** 205.
3. ——— and ——— .. "Two rippled-sheet configurations of polypeptide chains and a note about the pleated sheets," *Ibid.*, 1953, **39,** 253.
4. Low, B. W. and Grenville-Wells, H. J. — "Generalised mathematical relationships for polypeptide chain helices. The co-ordinates of the π-helix," *Ibid.*, 1953, **39,** 785.
5. Donohue, J. .. "Hydrogen-bonded helical configurations of the polypeptide chain," *Ibid.*, 1953, **39,** 470.
6. Rich, A. and Crick, F. H. C. "Structure of polyglycine, II," *Nature*, 1955, **176,** 780.
7. Sasisekharan, V. .. "Structure of poly-L-proline II," *Acta Cryst.*, 1959, **12,** 897.
8. ———. .. "Structure of poly-L-hydroxyproline A," *Ibid.*, 1959, **12,** 903.

THE RELATION BETWEEN ELECTROMAGNETIC AND GRAVITATIONAL INTERACTIONS*

BY S. THYAGARAJA RAO

(*Department of Physics, University of Madras, Madras-25*)

Received November 22, 1960

(Communicated by Prof. G. N. Ramachandran, F.A.SC.)

ABSTRACT

A new formulation of the electromagnetic interaction between charges is given using a relative interaction Lagrangian formalism. This leads to all the well-known effects in current electricity, but predicts, in addition, a variation of inertial mass with potential. In the analogous equations written for gravitation also, the inertial mass is changed by the potential energy. These equations are found to explain the gravitational phenomena usually explained by general relativity, namely, the precession of the Mercury perihelion, gravitational deflection of light and the red-shift. The agreement between theory and experimental observations is fair. The results are incorporated in Table I.

1. INTRODUCTION

IT is well known that we can start from a Lagrangian for the motion of a charged particle moving in a given electromagnetic field and work out the dynamics of its motion. Suppose the field is generated by the motion of a neighbouring charge, and we neglect retardation and back interaction, then the equations of motion lead to well-known effects in current electricity (such as magnetic force, induction by relative motion and acceleration). It is, however, possible to develop an alternative formulation in which the interaction part of the Lagrangian is dependent upon relative co-ordinates such as relative position, relative velocity, etc. This is worked out in this paper. It is found to lead to exactly the same magnitudes for all the usual effects in current electricity as the ordinary theory, except for terms of the order of v^2/c^2 which are negligible for current electricity. However, it leads to a variation of the inertial mass of the particle with its potential energy. Several interesting consequences arise from this new aspect of the theory. Thus, the equation may be adapted for gravitational fields, when it is found

* Prepared for presentation at the 25th Annual Session of the Indian Academy of Sciences, December, 1959.

to explain fairly well the precession of the planet Mercury, the deflection of light due to gravitational masses, and the occurrence of a red-shift.

In this paper we mainly deal with the results that are obtained from the approach in which one starts with a Lagrangian in which the interaction part depends only upon relative quantities. The arguments leading to this and related problems in current electricity will be presented in a subsequent paper from this laboratory.

2. FORMULATION OF THE PROBLEM

The usual Lagrangian is given by (Goldstein, 1953)

$$\mathrm{L} = \mathrm{T} + \frac{e_2}{c}\mathbf{A} \cdot \boldsymbol{v}_2 - e_2\Phi \tag{1}$$

where $\boldsymbol{v}_2$, e_2 represents the velocity and charge of the second particle. If the field is generated by a charge e_1, and if the retardation effects and back reaction are neglected, then

$$\mathbf{A} = \frac{e_1}{cr}\boldsymbol{v}_1; \quad \Phi = \frac{e_1}{r} \tag{2}$$

where $r = |\boldsymbol{r}_2 - \boldsymbol{r}_1|$. Substituting in (1) and writing the equation of motion, we have

$$\frac{d}{dt}(m_2\boldsymbol{v}_2) = \underset{(a)}{\frac{e_1e_2}{r^2}\hat{\boldsymbol{r}}} + \frac{e_1e_2}{c^2r^2}\Big[\underset{(b)}{\boldsymbol{v}_1(\boldsymbol{v}_2 \cdot \hat{\boldsymbol{r}})} - \underset{(c)}{\hat{\boldsymbol{r}}(\boldsymbol{v}_1 \cdot \boldsymbol{v}_2)} - \underset{(d)}{\boldsymbol{v}_1(\boldsymbol{v}_1 \cdot \hat{\boldsymbol{r}})}\Big]$$

$$- \underset{(e)}{\frac{e_1e_2}{c^2r} \cdot \dot{\boldsymbol{v}}_1}. \tag{3}$$

In this (a) represents the electrostatic force. (b) and (c) together represent the magnetic (Lorentz) force. (b) and (d) together give the effect of induction by relative motion and (e) the induction by acceleration of the particle producing the field.

Let us now take a Lagrangian in which the interaction part is purely relative,* as

$$\mathrm{L} = \mathrm{T} + \mathrm{L}_{\mathrm{int}} \tag{4 a}$$

* The arguments leading to such a formulation will be given in a subsequent paper.

where

$$L_{int} = -\frac{e_1 e_2}{r} - \frac{1}{2}\frac{e_1 e_2}{c^2 r} v^2 \tag{4 b}$$

and $v = v_2 - v_1$, the relative velocity of the particles. The equation of motion can be written as

$$\frac{d}{dt}(m_2 v_2) = \underset{(a)}{\frac{e_1 e_2}{r^2}\hat{r}} + \frac{e_1 e_2}{c^2 r^2}\Big[\underset{(b)}{v_1 (v_2 \cdot \hat{r})} - \underset{(c)}{\hat{r}\,(v_1 \cdot v_2)} - \underset{(d)}{v_1 (v_1 \cdot \hat{r})}\Big]$$

$$- \underset{(e)}{\frac{e_1 e_2}{c^2 r}\dot{v}_1} + \underset{(f)}{\frac{e_1 e_2}{c^2 r}\dot{v}_2} + \underset{(g)}{\frac{e_1 e_2}{c^2 r^2} v_2 (v_1 \cdot \hat{r})}$$

$$+ \underset{(h)}{\frac{1}{2}\frac{e_1 e_2}{c^2 r^2} v_1^2 \cdot \hat{r}} + \underset{(j)}{\frac{1}{2}\frac{e_1 e_2}{c^2 r^2} v_2^2 \hat{r}} - \underset{(k)}{\frac{e_1 e_2}{c^2 r^2} v_2 (v_2 \cdot \hat{r})}. \tag{5}$$

Terms (*a*), (*b*), (*c*), (*d*) and (*e*) are the same as before and represent the effect of current electricity. The new terms are (*f*), (*g*), (*h*), (*j*) and (*k*). We can show that if the particles form current-carrying closed circuits, then all these vanish when summed over the whole circuit except (*h*).

To start with, let us suppose that 1 is circuital and 2 is just an element. Then, since every element of 1 is electrically neutral, the terms (*f*), (*j*) and (*k*) vanish since the velocity of 2 alone is involved. (*g*) vanishes when integrated around 1. To see this, consider Fig. 1.

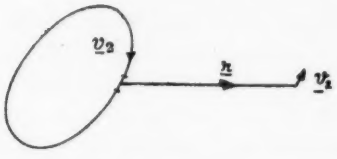


FIG. 1. Schematic diagram indicating the velocities (circuital) and v_1.

Here,

$$v_1 ds_1 = |v_1| ds_1.$$

Hence,

$$\oint_1 \frac{e_1 e_2}{c^2 r^2} v_2 (v_1 \cdot \hat{r})\, ds_1 = \frac{e_1 e_2}{c^2} v_2 |v_1| \oint_1 \text{grad}\left(\frac{1}{r}\right) \cdot ds_1$$

$$= \frac{e_1 e_2}{c^2} v_2 |v_1| \iint_{\Sigma} \text{and grad}\left(\frac{1}{r}\right) \cdot d\Sigma$$

$$= 0. \tag{6}$$

Term (h) can be shown to be negligible.

The order of the drift velocity responsible for ordinary currents of the order of 10 amperes/sq.mm. is very small. It is

$$v_1 = \frac{\text{current}}{\text{charge} \times \text{number density of electrons}}$$

$$\sim \frac{10 \times 10^2}{10 \times 10^{-20} \times 10^{23}}$$

$$\sim 10^{-1} \frac{\text{cm.}}{\text{sec.}}. \tag{7}$$

Thus, v_1^2/c^2 is of the order of 10^{-22}, and the term (h) is negligible compared to the electrostatic term (a). Thus, all the new terms vanish when we make the velocity $\boldsymbol{v}_1$ circuital and v_1 is small compared to c.

The terms (f) and (k) together can be brought to the left-hand side of equation (5) when this becomes

$$\frac{d}{dt}\left[\left(m_2 - \frac{e_1 e_2}{c^2 r}\right)\boldsymbol{v}_2\right] = \frac{d}{dt}[m_2' \boldsymbol{v}_2], \quad \text{say} \tag{7 a}$$

with

$$m_2' = m_2 - \frac{e_1 e_2}{c^2 r} = m_2 - \frac{V_2}{c^2} \tag{7 b}$$

where V_2 is the electrostatic potential energy at the position of the charge 2 due to the charge 1. Thus, the Lagrangian (4) implies a variation of the inertial mass with potential energy. The various consequences of this is the field of electromagnetism is reserved for a separate paper. Here, we shall consider the consequences of an exactly similar formulation for gravitational interactions.

3. GRAVITATIONAL EQUATIONS

The adaptation for gravitational fields may be obtained straight from equation (5). First, the quantity $e_1 e_2$ is replaced by $-GMm$. Let us further suppose that our problem is a two-body problem, in which one of the masses (M) is very massive (such as the Sun) and is at rest. Hence, $\boldsymbol{v}_1 = 0$ at all times and so $\dot{\boldsymbol{v}}_1 = 0$. Consequently, $\boldsymbol{v}_2 = \boldsymbol{v}$, and $m_2 = m$. Thus, Equation (5) reduces to the following:

$$\frac{d}{dt}(m\boldsymbol{v}) = -\frac{GMm}{r^2}\hat{\boldsymbol{r}}\left(1 + \frac{1}{2}\frac{v^2}{c^2}\right) - \frac{d}{dt}\left[\frac{GMm}{c^2 r}\boldsymbol{v}\right]. \tag{8}$$

This may be written in the form:

$$\frac{d}{dt}\left[m\left(1+\frac{GM}{c^2r}\right)\mathbf{v}\right]=-\frac{GMm}{r^2}\left(1+\frac{1}{2}\frac{v^2}{c^2}\right).\hat{\mathbf{r}}. \tag{9}$$

This is the fundamental equation. Here we find the effective mass is altered by the potential and is actually equal to $m - V/c^2$, where V is the potential energy as in the electromagnetic case. Starting from this equation we shall work out some of its consequences.

4. Gravitational Phenomena

(*a*) *Precession of Mercury.*—Taking the Lagrangian given in equation (5) adapted for our problem, using spherical polar co-ordinates and using the result that $v^2 = v_r^2 + r^2v_\theta^2 + r^2\sin^2\theta v_p^2$, we find that the Lagrangian does not involve the co-ordinate ϕ explicitly. Thus, ϕ is a constant for the problem. Hence, the orbit can be described by just two co-ordinates (r, θ) and it is planar.

We can write the equation of motion in polar co-ordinates as

$$\frac{d}{dt}\left[\gamma m_0\left(1+\frac{G_1M}{c^2r}\right)\frac{dr}{dt}\right]-\gamma m_0\left(1+\frac{G_1M}{c^2r}\right)r\left(\frac{d\theta}{dt}\right)^2$$

$$=-\frac{G_1Mm_0\gamma}{r^2}\left(1+\tfrac{1}{2}\frac{v^2}{c^2}\right)\left(1+\frac{G_1M}{c^2r}\right) \tag{10}$$

$$\frac{d}{dt}\left[\gamma m_0\left(1+\frac{G_1M}{c^2r}\right)r^2\frac{d\theta}{dt}\right]=0 \tag{11}$$

where

$$\gamma=\frac{1}{\left(1-\frac{v^2}{c^2}\right)^{\frac{1}{2}}}.$$

From (11) we have the result that

$$\gamma\left(1+\frac{G_1M}{c^2r}\right)r^2\frac{d\theta}{dt}=\text{constant, } k \text{ (say)}. \tag{12}$$

Using this in (10) and putting $u = 1/r$, we get the differential equation of the orbit as

$$\frac{d^2u}{d\theta^2}+u=\frac{GM}{k^2}+\frac{2G^2M^2}{k^2c^2}u+\frac{3}{2}\frac{GM}{c^2}\left[u^2+\left(\frac{du}{d\theta}\right)^2\right]. \tag{13}$$

We can show that the radial velocity does not contribute anything to the precession (*see* Appendix I) and so we can discard the $(du/d\theta)^2$ term in considering the precession of the orbit. Thus,

$$\frac{d^2u}{d\theta^2} + u = \frac{G_1M}{k^2} + \frac{2G^2M^2}{k^2c^2}u + \frac{3}{2}\frac{GM}{c^2} \cdot u^2. \tag{14}$$

It is easy to show that the second and third terms are very small compared to the first and hence can be taken to be perturbations on the Newtonian elliptic orbits. Let us take the more general case where

$$\frac{d^2u}{d\theta^2} + u = \frac{GM}{k^2} + \Sigma A_n u^n \tag{15}$$

where A_nu^n are all perturbation terms. Then we can readily show that the orbit is given by (*see* Appendix I)

$$u = \frac{GM}{k^2}\left[1 + e\cos\left\{\theta - \omega - \left[\sum \frac{1}{2} nA_n\left(\frac{G_1M}{k^2}\right)^{n-1}\right]\theta\right\}\right] \tag{16}$$

and the advance of the perihelion per rotation is given by

$$\Delta\theta_0 = \pi \sum nA_n\left(\frac{GM}{k^2}\right)^{n-1}. \tag{17}$$

Substituting in this from equation (14), we obtain for our problem

$$\Delta\theta_0 = \frac{5\pi G^2M^2}{k^2c^2}. \tag{18}$$

This gives a value of 35·5″ of arc per century for the planet Mercury, as compared with the observed value of 40·6″ (Sokolnikoff, 1956).

(*b*) *Deflection of light by gravitational mass.*—Let a photon of mass $m = h\nu/c^2$ pass near the Sun. We may calculate the deviation of the path as follows: For a photon, $v = c$ and so $\gamma \to \infty$. Thus from (12) we see that $k \to \infty$. Using this in (13) we get

$$\frac{d^2u}{d\theta^2} + u = \frac{3}{2}\frac{GM}{c^2}\left[u^2 + \left(\frac{du}{d\theta}\right)^2\right]. \tag{19}$$

The complementary function of this differential equation is $u = \cos\theta/R$ where R is the perpendicular distance between the initial path of light and

the centre of the gravitating mass. Using this, we can evaluate the R.H.S. and the particular integral is then 3/2. GM/c^2R. The solution is given by

$$u = \frac{3}{2}\frac{GM}{c^2R} + \frac{1}{R}\cos\theta. \tag{20}$$

Using Cartesian co-ordinates, we find for large y,

$$x = R - \frac{3}{2}\frac{GM}{c^2R}\cdot y. \tag{21}$$

Thus, the angular deviation is given by

$$\phi = \frac{3GM}{c^2R}. \tag{22}$$

This gives for a ray grazing the surface of the Sun a value of 1·31 seconds of arc for the gravitational deflection and the observed value ranges from 1·6″ to 1·75″. The Newtonian value is just 0·88″. All these are incorporated in a separate table (Table I).

TABLE I

Particulars	Classical theory	General relativity	Our formulation	Observation
1. Precession of the perihelion of Mercury	..	43″	35·5″	40·56″
2. Deflection of light	0·88″	1·76″	1·31″	1·6 to 1·75″
3. Red-shift ($\delta\lambda/\lambda$) ..	$\sim 10^{-6}$	$\sim 10^{-6}$	$\sim 10^{-6}$	$\sim 10^{-6}$

There is a more physical way of doing this. Let us take (9) and suppose that the momentum of the photon is given by mv. There is some difficulty in this since the effective inertial mass is $(m - V/c^2)$. Anyway, assuming this to be correct, and remembering that for a photon, the velocity does not change, we get from equation (9).

$$\frac{d}{dt}(\mathbf{p}) = -\frac{3}{2}\frac{GMm}{r^2}\hat{\mathbf{r}} + \frac{GMm}{c^2r^2}(\mathbf{v}\cdot\hat{\mathbf{r}})\mathbf{v}. \tag{23}$$

The component perpendicular to the line of flight is the relevant one and the parallel component vanishes by symmetry. Thus, we get

$$\Delta p = \int F_\perp \cdot \frac{dx}{c} = -\frac{3GMm}{cR}. \tag{24}$$

Thus,

$$\phi = \frac{|\triangle p|}{|p|} = \frac{3GM}{c^2R} \tag{25}$$

This is the same as obtained in (22).

(*c*) *Red-shift.*—Let a photon start from a point P, on the surface of the Sun. We require the change in its energy which is used up in doing work against gravitational attraction. Thus, we have to find the value of the integral

$$W = \int_P^\infty F_{\parallel} \cdot dx$$

$$= -\frac{1}{2}\frac{GMm}{R} . \tag{26}$$

This is independent of the point P on the surface from which the photon starts.

The question, whether the work done by the photon is equal to the change in its energy in this new dynamics, remain to be established. Thus, if we make use of the result that $m' = m - V/c^2$, and take $m' = h\nu'/c^2$ for a photon, then

$$\frac{\delta\nu}{\nu} = \frac{\delta\lambda}{\lambda} = \frac{GM}{c^2R} , \tag{27}$$

i.e., a value twice that given by the formulation given above which gives

$$\frac{\delta\nu}{\nu} = \frac{\delta\lambda}{\lambda} = \frac{W}{h\nu} = \frac{1}{2}\frac{GM}{c^2R} . \tag{28}$$

The value (27) agrees with that usually taken for the red-shift from General Relativity Theory.

The order of magnitude of this for the Sun is $\sim 10^{-6}$ and agrees with observations. It should be mentioned, however, that the experimental observations are not very reliable and give only an order of magnitude.*

ACKNOWLEDGEMENT

The author wishes to record his deep indebtedness to Prof. G. N. Ramachandran for his guidance and to the Atomic Energy Commission for financial assistance.

* With the advent of Mossbaeur effect, it may be possible to assess this value more accurately (Cranshaw *et al.*, 1960).

References

1. Goldstein, H. .. *Classical Mechanics*, Addison Wesley, 1953.
2. Eddington, A. S. .. *The Mathematical Theory of Relativity*, Cambridge University Press, 1952.
3. Sokolnikoff, I. S. .. *Tensor Analysis*, John Wiley, 1956.
4. Cranshaw, T. E., Schiffer, J. P. and Whitehead, A. B. *Phys. Rev. Letters*, 1960, **4**, 163.

APPENDIX I

Let us consider the orbit represented by the differential equation

$$\frac{d^2u}{d\theta^2} + u = \frac{GM}{k^2} + \sum A_n u^n + B\left(\frac{du}{d\theta}\right)^2. \tag{1.1}$$

We look for the solution which is correct to the first order in the eccentricity of the orbit. We adopt the standard method of successive approximation.

To start with, ignore the last two 'perturbing' terms. Then, the orbit is represented by

$$u = \frac{GM}{k^2}[1 + e\cos(\theta - \omega)] \tag{1.2}$$

(*see* Eddington, 1952). Using this on the L.H.S., we have

$$\frac{d^2u}{d\theta^2} + u = \frac{GM}{k^2} + \sum A_n \left(\frac{GM}{k^2}\right)^n (1 + e\cos(\theta - \omega))^n$$

$$+ B\left(\frac{GM}{k^2}\right)^2 e^2\cos^2(\theta - \omega).$$

We may omit terms involving e^2 and higher order terms. This immediately shows that, to this order of approximation, the radial component of velocity gives rise to no precession. Thus, we have

$$\frac{d^2u}{d\theta^2} + u = \frac{GM}{k^2} + \sum A_n \left(\frac{GM}{k^2}\right)^n$$

$$+ \sum A_n \left(\frac{GM}{k^2}\right)^n \cdot ne\cos(\theta - \omega) \tag{1.3}$$

The particular integral of this equation is

$$\sum A_n \cdot \left(\frac{GM}{k^2}\right)^n \cdot ne \cdot \frac{1}{2}(\theta - \omega)\sin(\theta - \omega)$$

$$= e\sin(\theta - \omega) \cdot \frac{GM}{k^2} \cdot \Delta\theta \tag{1.4}$$

where

$$\Delta\theta = (\theta - \omega)\frac{1}{2}\sum nA_n \left(\frac{GM}{k^2}\right)^{n-1}. \tag{1.5}$$

To this approximation the orbit is represented by the equation got by adding (1.5) to (1.2) and remembering that $\triangle\theta$ is small,

$$u = \frac{GM}{k^2}\,[1 + e\cos(\theta - \omega - \triangle\theta)]. \tag{1.6}$$

Thus the advance of perihelion per rotation is

$$\triangle\theta_0 = 2\pi \cdot \frac{1}{2}\sum nAn\left(\frac{G_1M}{k^2}\right)^{n-1}$$

$$= \pi \sum nAn\left(\frac{GM}{k^2}\right)^{n-1}. \tag{1.7}$$

This is the result used in the text.

363-61 Printed at the Bangalore Press, Bangalore City, by T. K. Balakrishnan, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.

NOTICE TO AUTHORS

Scientific papers intended for publication in the *Proceedings of the Indian Academy of Sciences* can be accepted only when they are communicated by a Fellow of the Academy whose duty shall be to satisfy himself that such communications are fit to be read at the Meeting of the Academy and published in its *Proceedings*.

Papers should not ordinarily exceed fifty pages of foolscap. MSS. should be either typewritten or written in legible hand on one side of the paper. All papers should be carefully revised by the authors and should be absolutely in final form for printing. Position for text-figures should be indicated. Each paper shall conclude with a critical summary not exceeding 350 words.

Drawings, diagrams or other illustrations should be made on larger scale (preferably) twice the size than the ones in which they are intended to appear. They should be done in Indian ink on bristol board with lettering in pencil. Scale of magnification of camera lucida tracings should be indicated by the side of drawings. In certain special cases arrangements will also be made for monochrome lithographic and other colour plates. Reduction of illustrations desired should be indicated in pencil. Appropriate legends should accompany all drawings. Names of authors are to be marked in pencil on the left-hand corner of drawing sheets. Photomicrographs should be securely mounted with colourless paste.

All tables, quotations and footnotes which will be set hereafter (beginning from Vol. I, No. 2) in types smaller than the text, should be typewritten on separate sheets and placed with the text in proper sequence. Footnotes should be numbered in Arabic numerals.

References to literature in the text should be given, whenever possible, in chronological order, only the names of authors and years of publication, in brackets, being given. They should be cited in full after the summary, the authors' names following in alphabetical order. Thus,

Name or Names of author; Name of Journal (abbreviation) with a single underline; Year of publication; Number of Volume with a double underline, and lastly page. The following would be a useful illustration:—

Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

Two copies of slip-proof and wherever possible, a page proof for final revision will be sent to authors. All corrections are best made on the slip-proof which should be transmitted to the Office of the Academy. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

Fifty free reprints including plates and with cover will be supplied for each paper. Additional copies can be supplied at cost on previous intimation.

Blocks appearing in the *Proceedings* will be available for purchase by their respective authors. Orders for the same should be sent along with the corrected proofs and in any case not later than one month after the date of publication of the paper. The price charged would be 25% of the actual cost of the blocks *plus* freight and despatching charges. If the blocks are reproduced in other journals or publications, due acknowledgment should be made in them to the *Proceedings*.

The original drawings and plates of blocks appearing in the *Proceedings* will be returned to such of the authors as may require them provided the cost of despatching such originals is borne by them.

CONTENTS

	PAGE
On the Possibility of a New Phase-determining Method Applying the Mössbauer Effect . . . . . R. Srinivasa Raghavan	265
Electron Spin Resonance Studies of the Free Radicals Derived from Tetra phenylhydrazine . . . . . M. Ramachandra Das, Arvind V. Patankar and Balu Venkataraman	273
Helical Conformations of Polypeptide Chains . . . . V. Sasisekharan	296
The Relation between Electromagnetic and Gravitational Interactions. . . . . . S. Thyagaraja Rao	323

1217

Library
THE UNIV. OF
OCT 12 1961
PHYSICS LIBRARY

Supplement to the
"Proceedings of the Indian Academy of Sciences"

INDEX TO VOL. LIII—(A)

AUTHORS' INDEX

Anantakrishnan, S. V. and Radhakrishnamurti, P. S. — Kinetic studies in ester hydrolysis, Part X, 28.

Bagavant, G. .. *See* Banerjee and Bagavant.

Balachandran, A. P. .. *See* Ramakrishnan and others.

Balasubramanian, C. .. *See* Venkateswarlu and Balasubramanian.

Balasubramanyam, K. .. Raman spectra of addition compounds of glycine (diglycine hydrochloride, diglycine hydrobromide and diglycine nitrate), 105.

Banerjee, D. K. and Bagavant, G. — Synthesis of the lactone of 2-carboxy-4-hydroxy-7-methoxy-1, 2, 3, 4-tetrahydrophenanthrone, 113.

Basu, B. K. and Srivastava, S. P. — On the logical and circuit design of the digital computer at T.I.F.R., Bombay, 44.

Bhamathi, G. .. *See* Ramakrishnan and others.

Bhargava, B. N. and Subrahmanyan, R. V. — A study of the pre-sunrise F-layer stratification at Kodaikanal, 227.

Bhat, A. N. and Jain, B. D. — 3-Acetyl-4-hydroxycoumarin as a reagent for the gravimetric determination of zirconium and titanium, 147.

Bhatnagar, P. L. .. On two-dimensional boundary layer in non-Newtonian fluids with constant coefficients of viscosity and cross-viscosity, 95.

Das, M. Ramachandra, Patankar, Arvind V. and Venkataraman, Balu — Electron spin resonance studies of the free radicals derived from tetraphenylhydrazine, 273.

Duggal, V. P., Rao, K. Raghavendra, Thapar, C. L. and Singh, V. — Anomalous reflections in a single crystal neutron spectrometer, 59.

Indumathi, S. .. *See* Ramakrishnan and others.

Jain, A. C. .. On compressible boundary layer on a flat plate with uniform suction, 12.

Jain, B. D.	..	*See* Bhat and Jain.
Krishnan, K.	..	The Raman spectra of organic compounds, Part I, 151.
Lagu, R. G. and Thosar, B. V.		Fluorescence and scintillation spectra of CsI (Tl) crystal, 219.
Masood, S.	..	Some theorems on self-reciprocal functions, 35.
Mathai, I. M.	..	Role of solvent in chemical reactions, Part IV, 73.
Patankar, Arvind V.	..	*See* Das and others.
Pillai, M. G. Krishna	..	*See* Venkateswarlu and others.
Radhakrishnamurti, P. S.	..	*See* Anantakrishnan and Radhakrishnamurti.
Ramachandran, G. N.	..	On faltung and correlation of functions and their application in physical problems, 123.
Ramakrishnan, Alladi, Balachandran, A. P. and Ranganathan, N. R.		Some remarks on the structure of elementary particle interactions, 1.
Ramakrishnan, Alladi, Bhamathi, G. and Indumathi, S.		A limiting process in quantum electrodynamics, 206.
Ramaswamy, K.	..	*See* Venkateswarlu and others.
Ranganathan, N. R.	..	*See* Ramakrishnan and others.
Rangaswami, S. and Sambamurthy, K.		Chemical examination of the leaves of *Rhododendron campanulatum* D. Don., 98.
Rao, B. N. Subba	..	Photoelectron scintillation spectrometer and the conversion coefficient of the 279 Kev. transitions in Tl^{203}, 244.
Rao, K. Raghavendra	..	*See* Dnggal and others.
Rao, S. K. Lakshmana	..	On the relation extrema of the Turán expression for Bessel functions, 239.
Rao, S. Thyagaraja	..	The relation between electromagnetic and gravitational interactions, 323.
Sambamurthy, K.	..	*See* Rangaswami and Sambamurthy.
Sasisekharan, V.	..	Helical conformations of polypeptide chains, 296.
Singh, V.	..	*See* Duggal and others.
Sivarajan, S. R. and Vold, R. D.		Micellar size and shape in solutions of calcium stearate in cetane from optical depolarization data, 136.

Srinivasan, R. .. The significance of the phase synthesis, 252.

Srinivasa Raghavan, R. .. On the possibility of a new phase-determining method applying the Mössbauer Effect, 265.

Srivastava, S. P. .. *See* Basu and Srivastava.

Subrahmanyan, R. V. .. *See* Bhargava and Subrahmanyan.

Sundara Rajan, A. .. Microwave spectrum of trichloroacetonitrile, 89.

Thapar, C. L. .. *See* Duggal and others.

Thosar, B. V. .. *See* Lagu and Thosar.

Venkataraman, Balu .. *See* Das and others.

Venkatasubramanian, N. .. Studies in oxidation : Oxidation of some aromatic secondary alcohols with chromium (VI) oxide—Part II, 80.

Venkateswarlu, K. and Balasubramanian, C. .. Solvent effect on $C \equiv N$ vibration in Raman Effect, 202.

Venkateswarlu, K., Pillai, M. G. Krishna and Ramaswamy, K. Intensity studies in Raman Effect—Positional isomerism, 195.

Viswanathan, K. S. .. The correlated Hartree-Fock equations and the generalised density matrices, 169.

Vold, R. D. .. *See* Sivarajan and Vold.

Waghmare, T. R. .. Charge distribution of the proton, 214.

TITLE INDEX

Bessel functions, on the relative extrema of the Turán expression for (Rao), 239.

Boundary layer, compressible, on a flat plate with uniform suction (Jain), 12.

Boundary layer, two-dimensional, in non-Newtonian fluids with constant coefficients of viscosity and cross-viscosity (Bhatnagar), 95.

Computer, digital, at T.I.F.R., Bombay, on the logical and circuit design of (Basu and Srivastava), 44.

Correlated Hartree-Fock equations and the generalised density matrices (Viswanathan), 169.

Electromagnetic and gravitational interactions, the relation between (Rao), 323.

Electron spin resonance studies of the free radicals derived from tetraphenylhydrazine (Das and others), 273.

Elementary particle interactions, some remarks on the structure (Ramakrishnan and others), 1.

Faltung and correlation of functions and their application in physical problems (Ramachandran), 123.

Fluorescence and scintillation spectra of CsI (Tl) crystal (Lagu and Thosar), 219.

Helical conformations of polypeptide chains (Sasisekharan), 296.

Kinetic studies in ester hydrolysis, X (Anantakrishnan and Radhakrishnamurti), 28.

Lactone of 2-carboxy-4-hydroxy-7-methoxy-1, 2, 3, 4-tetrahydrophenanthrone (Banerjee and Bagavant), 113.

Micellar size and shape in solutions of calcium stearate in cetane from optical depolarization data (Sivarajan and Vold), 136.

Microwave spectrum of trichloroacetonitrile (Sundara Rajan), 89.

Neutron spectrometer, single crystal, anomalous reflections in (Duggal and others), 59.

Oxidation, studies in: Oxidation of some aromatic secondary alcohols with chromium (VI) oxide, Part II (Venkatasubramanian), 80.

Phase-determining method, new, applying the Mössbauer Effect, on the possibility of (Srinivasa Raghavan), 265.

Phase synthesis, the significance of (Srinivasan), 252.

Photoelectron scintillation spectrometer and the conversion coefficient of the 279 Kev. transitions in Tl^{208} (Rao), 244.

Pre-sunrise F-layer stratification at Kodaikanal, a study of the (Bhargava and Subrahmanyan), 227.

Proton, charge distribution of (Waghmare), 214.

Quantum electrodynamics, a limiting process in (Ramakrishnan and others), 206.

Raman Effect, intensity studiesin—positional isomerism (Venkateswarlu and others), 195.

Raman Effect, solvent effect on C ≡ N vibration in (Venkateswarlu and Balasubramanian), 202.

Raman spectra of addition compounds of glycine (diglycine hydrochloride, diglycine hydrobromide and diglycine nitrate) (Balasubramanyam), 105.

Raman spectra of organic compounds, I (Krishnan), 151.

Rhododendron campanulatum D. Don., leaves of, chemical examination of (Rangaswami and Sambamurthy), 98.

Self-reciprocal functions, some theorems on (Masood), 35.

Solvent, role of, in chemical reactions, IV (Mathai), 73.

Zirconium and titanium, gravimetric determination, 3-acetyl-4-hydroxy-coumarin as a reagent for (Bhat and Jain), 147.